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A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

WILLIAM CROOKES, F.R.S., &c.

VOLUME LXXIII.—1896.



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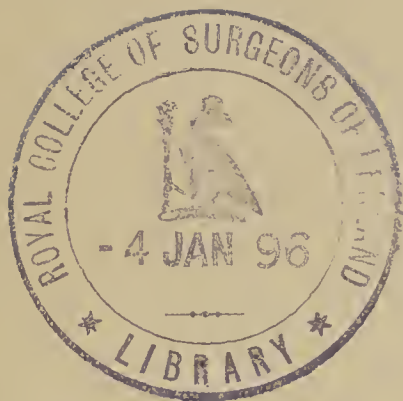
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THE CHEMICAL NEWS.

VOLUME LXXIII.

EDITED BY WILLIAM CROOKES, F.R.S., &c.

No. 1884.—JANUARY 3, 1896.

NOTE ON THE
ANALYSIS OF CHROME-IRON ORE, FERRO-
CHROMIUM, AND CHROME STEEL.

By Dr. S. RIDEAL and S. ROSENBLUM.

ABOUT 1820 chrome ores were first introduced in considerable quantities for the manufacture of chromium salts, and naturally the quantitative determination of the amount of metallic chromium contained in them received much attention at the hands of chemists.

Calvert 1852 (1), Bunsen 1854 (2), and Woehler (4) some years later were the first to devise satisfactory quantitative methods for the analysis of chrome ores, but these methods were very incomplete and would hardly satisfy the modern chemist.

Since then chromium has taken a very prominent place in chemical industry, and the literature referring to the determination of it has increased in proportion to its use in the production of various salts, chrome paints, ferro-chromium, chrome-steel, &c.

The list of papers on this subject which we have selected, and which, as regards the analysis of chrome-steel, is still far from being complete, will give some idea of the importance of the subject and of the number of eminent chemists who have made a special study of it.

In the proposals which have been made for the quantitative analysis of the chrome ore or of ferro-chromium, the chief difficulty has been in obtaining a convenient method for rendering the chromium soluble. The gravimetric methods of determining the chromium from its solutions were soon abandoned as requiring too much time, and two volumetric methods, viz., the permanganate method of H. Schwartz ("Fresenius Quantitative Anal.," i., § 112, 2a), and the bichromate method of Penny ("Fresenius Quantitative Anal.," i., § 112, 2b) have since been universally adopted.

The chief problem, viz., the complete decomposition of the ore or of its iron alloy remained for a long time unsolved, and the most widely differing methods have from time to time been proposed for this purpose. It was soon found that a wet decomposition by means of acids in combination with oxidising agents would not produce the desired effect, so that almost all the subsequent methods which were proposed for the decomposition of chrome ores or alloys are based on the oxidising action of mixtures containing in varied proportions and combina-

tions Na_2CO_3 , K_2CO_3 , KNO_3 , KClO_3 , KHSO_4 , KF , $\text{Na}_2\text{B}_4\text{O}_7$, &c., &c.

Some of these methods gave satisfactory results, and have found a very extensive application, as, for instance, the so-called magnesia-method of Dr. J. Clark (14), which was proposed by him as early as 1871.

It may be interesting to mention that six years later Christomanos (20) proposed the above mentioned method as one which had been carefully worked out by himself, for the decomposition of chrome ores. He communicated the very accordant results of about 50 different chrome ores, and thus once more proved the exactness of the magnesia-method, the priority of which undoubtedly belongs to Dr. J. Clark. Another reagent for the decomposition of chrome ores has lately been proposed by J. E. Stead (32). It is the so-called tri-basic reagent, consisting of a mixture of 4 parts lime, 1 part Na_2CO_3 , and 1 part K_2CO_3 , which readily effects a complete decomposition. A very similar mixture, viz., 2 parts Na_2CO_3 + 3 parts $\text{Ca}(\text{OH})_2$, was proposed in 1876 by Dr. R. Kayser (17). In all the methods suggested for the decomposition of chrome ores and alloys special stress was laid upon rendering the time required for complete decomposition as short as possible, and this point, as far as the work-analyst is concerned, is naturally of great importance.

The methods previously mentioned fulfilled this condition in so far that they reduced the time necessary for complete decomposition from about 4 hours to 1 to 2 hours.

With the introduction of sodium peroxide for laboratory use the decomposition of chrome ores and alloys enters into a new phase, and W. Hempel (34) was the first to draw the attention of chemists (in 1893) to the use of this reagent for effecting the decomposition of chrome ores. The experiments which he made were only of a qualitative nature, but during the same year J. Spueller and S. Kalman (35) in Germany and Dr. J. Clark (36) in this country adopted sodium peroxide for the quantitative analysis of chrome ores and alloys, and especially the two first-named chemists succeeded in working out an exact method for the analysis of chrome ore, ferro-chromium, and chrome steel.

The chief claim made for the sodium peroxide was the extraordinary rapidity with which a complete decomposition could be effected, provided that the ore was reduced to a very fine powder.

E. H. Saniter (40) has quite recently also published a

paper upon the subject. In this paper he does not refer to the process of Kalman and Spueller, which we have found to give satisfactory results, and describes his process as "A New Method for the Analysis of Chrome Ore and Ferro-chromium," although it is practically only a modification of Dr. Clark's process. He further states that 3 to 5 minutes are sufficient to decompose even a "moderately finely ground" chrome ore, the very fine grinding thus becoming quite unnecessary. Considering the considerable importance which such an easy and exact way of determination would have for the chromium industry, we thought ourselves justified in undertaking a careful inquiry into the above mentioned methods, and in a recent paper read before the Society of Chemical Industry we have communicated the results at which we have arrived.

We find as a result of this inquiry that sodium peroxide can be used for effecting the fusion of a chrome ore or ferro-chromium if it be reduced to a very fine powder, and that the heating with sodium peroxide must be continued for five minutes in the case of chrome-iron ores, and ten minutes in the case of ferro-chromes. In both cases it is advisable to add a second quantity of sodium peroxide after the melt has partially cooled and then re-heated. After fusion it is essential that the aqueous solution of the melt should be boiled before acidulation for ten minutes in order to effect the complete decomposition of any sodium peroxide which remains still unreduced.

Before titrating the solution, it is desirable to filter from any oxides of iron or nickel which may be present, since the latter interferes with the end reaction when ferricyanide is used as an indicator. We submit a summary of the papers bearing on this subject which may be of value to those readers of the *CHEMICAL NEWS* who are interested in the analysis of these chromium compounds.

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RAPID DETERMINATION OF NITRIC NITROGEN IN VEGETABLE PRODUCTS.

By P. PICTET.

THE method of determination in question depends on the colouration taken by brucine on contact with nitric acid, free or liberated from a nitrate by the action of concentrated sulphuric acid. A drop of the liquid containing the nitrate is placed upon a plate of porcelain, and there is mixed with it a drop of pure concentrated sulphuric acid. Some fragments of brucine are allowed to fall into the liquid, which is successively diluted with distilled water, the dilution being increased until the colouration ceases to be produced. The method permits of the determination of 1 part of nitric nitrogen in 50,000 parts of water.

Modus operandi.—The organic matter is dried in the stove at 100°, and then finely powdered. We weigh off 2 or 4 grms., according to the supposed proportion of nitric acid. The powder is placed in a small flask with a long narrow neck, and there are added 20 c.c. of distilled water. The flask is rapidly heated to near upon ebullition, so as to avoid the loss of liquid in the state of vapour. At this moment the flask is sealed hermetically, and it is shaken from time to time for a quarter of an hour, leaving the flask in a hot place so as to dissolve the nitrate completely. When cold, we filter the liquid through a layer of animal charcoal, powdered and washed, and resting at the bottom of a funnel on a small plug of asbestos, not too compact. The clear colourless filtrate is received in a small flask which supports the funnel. During filtration the funnel is covered with a slender plate of glass. We thus collect from 10 to 15 c.c. of liquid. The flask is then sealed hermetically until the moment of determination.

For determination we take, with a graduated pipette, exactly 2 c.c. of the liquid, which is transferred to a testing-glass holding 50 to 60 c.c. With a cylindrical glass rod of 3 m.m. in diameter, rounded at its end, we take a drop of the liquid and deposit it upon a plate of white porcelain laid on a horizontal support. With a similar rod, we take from a bottle a drop of pure monohydrated sulphuric acid. We allow this drop to fall carefully upon the nitric liquid and mix the two liquids intimately with a stout platinum wire, spreading them out to the diameter of a 50 centimes coin. Then we throw suddenly into the middle of the liquid, with the point of a penknife, a particle of finely powdered brucine of the

size of a pin's head. An intense red colour at once appears and spreads concentrically. Into the glass we add gradually 2 c.c. of distilled water until the colouration no longer appears. We then make a second more accurate determination, proceeding near the limit by fractions of a c.c. of water.

With a little practice the first determination can be made very rapidly.

Calculation of the Proportion of Nitric Nitrogen.—Let 2 grms. of the dry pulverised substance be digested with 20 c.c. of water. In the assay, in order no longer to obtain a perceptible red tint, we have been obliged to add to 2 c.c. of the solution 10.4 c.c. of water. The volume then becomes $2 + 10.4 = 12.4$ c.c. This liquid contains per c.c. 0.0000207 of nitric nitrogen. But the quantity of this liquid which corresponds to one grm. of solid matter is—

$$12.4 \text{ c.c.} \times \frac{10}{2} = 62 \text{ c.c.}$$

The nitric nitrogen in 1 grm. of the substance is $0.0000207 \times 62 = 0.00128$ grm., or 0.128 per cent.

Determination in presence of a Nitrite.—A nitrite in solution gives the same colouration with brucine and sulphuric acid. Along with the known means for detecting nitrous acid, we may mention pure concentrated hydrochloric acid not containing free chlorine, employed in the same manner as sulphuric acid. It decomposes the nitrites without attacking the nitrates, and enables us to detect with brucine a nitrite in presence of a nitrate.

If we wish to determine nitric nitrogen accurately, we search first for the presence of nitrous nitrogen and determine it by the ordinary methods (Trommsdorf, Griess, Piccini). Then, in testing for brucine with sulphuric acid, when the colouration has diminished in intensity by dilution, we add to the drop of the solution a minute drop of chlorine water, taken with a platinum wire, and mix intimately. After three minutes we add sulphuric acid and then brucine. The action of the chlorine upon the nitrite is very rapid, almost instantaneous, if the nitrite is not very dilute. A slight excess of chlorine does not interfere, and hydrochloric acid is not injurious.

This last experiment shows the totality of the oxidised nitrogen. The presence of a sulphite, a sulphide, or an acetate does not attenuate the colour of the brucine.—*Comptes Rendus*, cxxi., p. 758.

THE TREATMENT OF THE EMERALD AND THE PREPARATION OF PURE GLUCINA.

By P. LEBEAU,

THE procedures used for extracting glucina from the emerald are numerous, but for the most part rather delicate; this mineral being not attackable by acids and containing a large proportion of silica. As the presence of this last substance always complicates the separation of the metallic oxides, we have selected a method which permits of its elimination at the outset in the state of silicon fluoride.

Woehler has often used for attacking silicated minerals the hydrofluoric acid produced in the presence of the pulverised mineral by the action of sulphuric acid upon calcium fluoride. Other acids have replaced the use of the hydrofluorate of a fluoride or of alkaline fluorides.

The Attack of Emerald.

1. On applying Woehler's procedure to the treatment of the emerald, we find that it is difficult to obtain a complete action, especially when using rather considerable quantities of material. This defect may be remedied by melting the emerald at first with calcium fluoride. To this end, we heat from 5 to 6 kilos. of a mixture of 1 part

emerald with 2 parts of calcium fluoride in a large crucible of graphite with a coke fire. When the mass is fluid, it is poured into a trough filled with water, yielding thus a porous material easily pulverised. The attack with sulphuric acid is very brisk, and must be effected in the cold. It is convenient to operate in a large dish of stoneware. When the escape of silicon fluoride has ceased, we heat on the sand-bath until there appear abundant white fumes of sulphuric acid. We then throw it into water by small portions, when aluminium, iron, and glucinum sulphates pass into solution, and there is formed a white deposit of calcium sulphate. The liquid is decanted, the precipitate is washed, and the solutions are concentrated. The excess of acid is then partially saturated with potassium carbonate and the liquid is allowed to cool, when there ensues an abundant deposit of alum, which carries down the chief part of the alumina. The mother-liquors separated from the alum are saturated with ammonia with the further addition of an excess of ammonium carbonate, which is left in contact for some days with frequent stirring. The filtrate on ebullition deposits an impure glucinum and ammonium carbonate, to the purification of which we shall return below.

2. The use of the electric furnace supplies a new and expeditious method for the treatment of the emerald. This mineral if heated in a coke tube readily melts and enters into ebullition. There are disengaged abundant vapours consisting at the outset of almost pure silica, which is deposited as a thick lining at the end of the tube. When, after the experiment, we examine the deposits nearer the heated part we find that their proportion of silica diminishes, though it is still higher than the quantity normally present in the emerald. On the other hand, the more fixed part contains only about half the silica of the emerald, or a mean of 30 per cent. If we operate in a crucible, and stop the heating when the escape of silica—very abundant at first—begins to slacken, there remains a fused substance, always containing a small quantity of lime derived from the furnace, and having the property of becoming pulverised on cooling like potassium bichromate. This silicate, which is more basic than emerald, is directly attackable by acids. We may, *e.g.*, decompose it by hydrofluoric and sulphuric acids, and obtain a solution of sulphates which may be treated as indicated above.

Purification of the Glucina.

The impure glucinum and ammonium carbonate is redissolved in nitric acid, and the dilute solution is mixed with a little potassium ferrocyanide, which throws down all the iron.

We filter, then remove the excess of ferrocyanide by means of copper nitrate; the copper being finally eliminated by means of a current of hydrogen sulphide; we have thus a solution of glucinum nitrate free from iron. It is then only required to separate the alumina which was carried down in the first solution in ammonium carbonate.

To remove these last traces of alumina, we have utilised the property of aluminium hydroxide of being easily polymerised even in the cold, and of thus becoming much less easily attackable by reagents. If we allow the precipitate of hydroxide obtained on treating ammonium nitrate or sulphate with ammonia to remain in the liquid in which it has been formed, it loses its gelatinous aspect and becomes much less easily soluble in acids. It is then completely insoluble in ammonium carbonate.

Glucina free from iron is precipitated from its nitric solution by ammonia. It is left to settle for three or four days, the supernatant liquid is decanted away and is replaced by a concentrated solution of ammonium carbonate, which slowly dissolves the glucina, leaving a slight white deposit of alumina.

The filtrate is heated to ebullition, and the precipitate thus formed is carefully washed and dissolved in pure nitric acid. On evaporating and igniting the solution we

obtain glucina in a dense absolutely pure form. M. Deslandres has kindly examined its spectrum, and has found in it no other metal.—*Comptes Rendus*, cxxi., p. 641.

PROGRAMME OF THE BATAVIAN SOCIETY OF EXPERIMENTAL PHILOSOPHY, OF ROTTERDAM.

AMONG the questions proposed for examination, the following may have a special interest for our readers :—

4. *Question 130.*—An exposition of the anatomical and chemical composition and the vital functions of one, or of more, species of a family of plants represented in Holland or in some of its colonies, and as yet not examined.

6. *Question 141.*—An exact critical review of what is known on the volcanic phenomena of the Indian islands.

9. *Question 154.*—What mode of heating large buildings is the best, most economical, and most sanitary?

10. *Question 155.*—An experimental research into the causes of phosphorescence, especially in the lower animals.

11. *Question 156.*—An experimental research on the electrical properties of some metallic alloys.

14. *Question 164.*—An exact determination of the indices of refraction of similar substances in different parts of the spectrum, and of the absorption spectrum of the same substances.

16. *Question 166.*—An examination of the specific heat of rhombic sulphur above 100°; of monoclinar and amorphous sulphur at different temperatures; of red phosphorus above 100°; and of common phosphorus at different temperatures.

21. *Question 176.*—Monographs on an element, *e.g.*, sulphur; on a class of its combinations; on its compounds with oxygen and carbon; on a phenomenon or series of phenomena, such as the action of sulphuric or nitric acid upon other bodies.

22. *Question 177.*—Very careful experimental determination of the atomic weight of at least one element not as yet sufficiently known.

24. *Question 181.*—A description of the vital conditions and properties of one or more species of moulds, ferments, or bacteria which are important in agriculture, horticulture, in the production of butter, cheese, beer, vinegar, alcohol, &c.

31. *Question 188.*—How long do the bacilli of tuberculosis remain virulent in milk, and especially in butter-milk, under the ordinary conditions of trade?

32. *Question 189.*—How long do pathogenic bacteria originating in the intestinal canal remain virulent in potable waters not sterilised, in flowing waters, in ditch-waters, and well-water?

33. *Question 190.*—A chemical and bacteriological investigation of the water of a river into which flows the sewage water of a great city.

35. *Question 192.*—A research on the origin and physiological signification of the green colouring matter in the bodies of green articulata (animals).

36. *Question 193.*—New researches on the action of sulphur in powder or salts of copper on the disease-parasites of plants.

37. *Question 194.*—A research on the part played by micro-organisms in the transformation of vegetable matter in the soil into humus.

The Society's Gold Medal, of the weight of 30 ducats, will be awarded to the author of the best reply to any of these questions.

The papers must be drawn up in Dutch, French, English, German, or Latin written in Italian characters, in another handwriting than that of the author, and not signed by him, but marked with a motto, and accom-

panied by a sealed envelope bearing the same motto and enclosing the name and address of the author.

The documents must be sent post free to the Chief Secretary, Dr. G. J. W. Bremer, on or before February 1, 1897.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, December 10th, 1895.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Nov. 1st to Nov. 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined three were recorded as "clear but dull," the remainder being clear, bright, and well filtered.

We have this month to record a large excess of rainfall, the quantity measured at Oxford being 4'17 inches, as compared with 2'31 inches (the average for 25 years), showing an excess of 1'86 inches. The rain was chiefly confined to the first half of the month, three-fourths falling during the first fifteen days; there were thirteen days on which no rain fell.

It is satisfactory to be able to report that the Thames-derived waters show a marked improvement in quality when the analyses for the past month are compared with the results for the corresponding period of last year. The Autumnal floods invariably cause a slight increase of colour, and the organic carbon is correspondingly raised.

Our bacteriological examinations give the following numbers of colonies per c.c.

	Colonies per c.c.
Thames water, unfiltered	7400
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	120
Ditto ditto lowest	44
Ditto ditto mean	88
New River water, unfiltered .. -- ..	5000
New River water, from the Company's clear water well	70
River Lea water, unfiltered	2000
River Lea water from the East London Com- pany's clear water well	52

These results show a very high efficiency in the methods of filtration employed by the Water Companies, and that the quality of the supply is excellent.

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from vol. lxxii, p. 313).

Chloride of Potassium from Chloroplatinate of Potassium.

HAVING proved the possibility of purifying chlorate of potassium from all solid impurities, I turned my attention to producing chloride from chloroplatinate of potassium made from chlorate which could be completely volatilised. My object in so doing was to check my previous estimates of the molecular combination of silver with chloride of potassium, and satisfy myself, at the same time, that this chloride was homogeneous.

I prepared the chloroplatinate by the method of fractionating adopted by M. Bunsen for separating potassium, caesium, rubidium, and sodium.

I had procured a very large quantity of chlorate of potassium, freed from foreign metals by the method of successive crystallisations, as I have described on page 663 of my "New Researches on the Laws of Chemical Proportions." The chloride made from it left, on volatilisation, one five hundred thousandth part of silica mixed with silicate of potassium and sodium. Moreover it gave, on spectrum analysis, persistent signs of the presence of this last metal.

I have subjected upwards of half a kilogram. of this purified chlorate, in a large platinum distilling apparatus, to three more crystallisations in water made alkaline by 0.1 per cent of hydroxide of potassium made from pure nitre, and containing traces only of sulphide of potassium. I performed the solutions, crystallisations, filtrations, and washings with pure water, in enclosed and purified air as much as possible, taking all the precautions mentioned above, and especially preventing the air from the laboratory passing into the room where I was working, or the air from this room passing into the platinum apparatus.

The chlorate did not show the sodium line after the third treatment, and the chloride which it formed by dissociation was volatilised without leaving any residue.

I re-dissolved the chlorate a fourth time, but in pure water, so as to make certain of removing all the hydroxide of potassium used. I thus obtained about one hundred and fifty grms. of pure salt, which was at one operation reduced to the state of chloride, by warming it with the greatest care in a large platinum retort with a domed top, and making the arrangements described above, to satisfy myself whether the dissociation was taking place without evolving chlorine. As a matter of fact, I found that the chlorate was transformed into chloride without liberating a trace of chlorine.

The resulting chloride was neutral to litmus paper; on spectrum analysis it did not show a trace of the sodium line, and it coloured a Bunsen flame deep blue. I have dissolved it in 2 litres of pure water condensed in a platinum coil,* and I have poured the solution into a platinum distilling apparatus holding 5 litres, which could be closed with a platinum plug to prevent access of air to it.

Chloride of Platinum.

I have prepared chloride of platinum as pure as it is possible to get it. To do this I dissolved 150 grms. of platinum

(freed from iridium, rhodium, iron, and silica in fine flakes, by boiling in hydrochloric acid) in pure aqua regia, held in a Sèvres dish, underneath a glass funnel with its edges turned inwards, thus making a gutter, to which was soldered an open tube meant to carry off the liquid condensed from the fumes given off by aqua regia when attacking the metal, and while evaporating the platinum solution to dryness. The residue was dissolved in pure water. It was dissolved and evaporated three separate times, to eliminate, as much as possible, the nitrous compounds which it obstinately retained.

Whilst the platinum was being dissolved, evaporated, and re-dissolved, the dish and the funnel condenser which held the products were kept in a closed glass case communicating with a ventilating chimney.

The chloride of platinum was brownish red when solid; it dissolved in water, making a clear but reddish yellow solution. Fearing that some platinoso-platinic chloride was present, I raised the solution to boiling point, and passed a current of washed chlorine through it, by means of a tube through the spout of the funnel, until it was sufficiently concentrated, owing to which it became of an intense orange-yellow colour. Having reached this result I cut off the current of chlorine, and kept the solution at 100° until it ceased to smell of chlorine.

Directly after it was prepared I put the solution into a Bunsen flame, on the end of a fine platinum wire, recently heated to redness; spectrum analysis of the flame showed the sodium line, until the platinum liberated by reducing the chloride was brought to incandescence. A repetition of the experiment in a hydrogen flame gave the same result. I did not see any other lines.

The air of the glass case in which I carried on the operations had then brought some sodium to the chloride, because the materials used in preparing it were quite free from this impurity.

Whatever might be the source of the sodium, I added pure water to the platinic solution, so as to make a solution with 10 per cent of chloride.

Chloroplatinate of Potassium.

To the platinic solution I added, little by little, stirring it all the time, a sufficient volume of chloride of potassium to change about four-tenths of the dissolved potassium compound into chloroplatinate, and I left the precipitate in the filtrate for twelve hours, taking care to keep the precipitate in suspension: this was accomplished by removing the platinum plug and stirring the contents.

Modifications of Chloroplatinate of Potassium.—The clear solution was poured off into a large covered platinum vessel. It was a deeper yellow than a cold aqueous solution of chloroplatinate of potassium. I noticed this on several occasions—on precipitating, when cold, an excess of a weak solution of potassic chloride by platinic chloride. It suffices to boil the strongly coloured solution; then, by cooling, either quickly or slowly, the liquid loses a great deal of its colour, and at the same time deposits very brilliant, citron-yellow, granular chloroplatinate.

I found the same thing, in a greater degree, when using platinic chloride to precipitate a cold supersaturated solution of chloride of ammonium. The liquid was coloured deep pure yellow; after boiling it, and leaving it to cool, it became quite colourless, depositing orange-yellow crystals of chloroplatinate of ammonium mixed with crystals of sal-ammoniac: this can be easily verified by putting it all into a half-saturated solution of chloride of ammonium, which dissolves the sal-ammoniac without touching the chloroplatinate of ammonium.

There are therefore two varieties of chloroplatinate of potassium and chloroplatinate of ammonium: these are distinguished by their physical state and their relative solubility. These variations are due to the temperature at which these salts of chlorine are formed. If formed when cold, they are flocculent, dull yellow, and distinctly

* The water used for solutions and washing was condensed in a platinum coil, and kept for use in a very large platinum flask with a platinum stopper. This water was made from spring water distilled in succession:—1st, with a great excess of a very alkaline solution of permanganate of potash, to destroy organic matters; 2nd, with a solution of sulphate of alumina, to eliminate the traces of ammonia always present in water distilled with permanganate; 3rd, alone, to keep back the traces of sulphate of alumina mechanically mixed with its vapour. During the first two distillations the water vapour was condensed in a tin refrigerator. It was only at the third distillation that I used the platinum coil, the upper part of which was turned back and reached far into a socket soldered on to the lid of the distilling chamber, and the lower part was also turned up and passed into the large platinum flask used to store the pure water.

soluble in saturated solutions of the alkaline chlorides of which they are partly formed,

If formed at about 100° , these compounds are always granular, crystalline, scarcely soluble when cold in saturated solutions of alkaline chlorides, and are entirely separated, by cooling, from boiling saturated solutions of these chlorides, and especially from chloroplatinate of ammonium.

To return to the precipitated chloroplatinate of potassium left in the platinum apparatus; it was flocculent and of a dull yellow colour. It was distinctly soluble in pure water, colouring it yellow; I put the pasty mass, with the washings from the dish, into a covered platinum retort, and then washed the precipitate by decantation. I continued the washing until the yellow water poured off—when properly concentrated by boiling, cooling, and separating from the crystallised chloroplatinate—*was no longer precipitated by a ten per cent solution of platinic chloride.*

The washing, in the end, had robbed the solution of nearly half the volume of flocculent chloroplatinate made. I noticed, moreover, that during the washing the compound changed slowly from the flocculent to the granular state.

Before proceeding to desiccation, which was done in a covered platinum vessel, sheltered as far as possible from the surrounding air, I took care to put a piece of the chloroplatinate, on a fine platinum wire loop, in a hydrogen flame; it coloured it *greenish blue* from the beginning until the platinic chloride was completely decomposed. The flame then changed to violet-blue. Spectrum analysis of the flame showed, with the potassium spectrum, the sodium line more intense than in a hydrogen flame burning in air at the same time.

On desiccating it at 100° the chloroplatinate was greatly reduced in bulk, and its colour changed to a very brilliant citron-yellow. It was kept in a covered platinum dish, under a bell-jar with *ground and greased* edges, on a smooth sheet of glass, until it was required for reducing in a hydrogen flame.

The washings from the chloroplatinate were added to the filtrate. This liquid, which amounted to about $2\frac{1}{2}$ litres, contained almost *two-thirds* of the chlorate of potassium experimented on.

The liquid, being too much diluted with water to precipitate the amount of chloride of potassium I wished to recover from it, by the addition of 10 per cent of the platinic chloride solution, I concentrated it in the same apparatus, and reduced its volume to about 1350 c.c.

During the concentration a noticeable amount of chloroplatinate of potassium was deposited, and the amount of it increased still more on cooling. I then added to the liquid, little by little, a 10 per cent solution of platinic chloride equal in volume to that used in the first case. I kept the flocculent precipitate suspended in the liquid for a whole day. After this it was left quiet. I then poured off the supernatant liquid, which was strongly tinged with yellow, and proceeded to wash the flocculent chloroplatinate in the platinum retort, exactly as described for the first precipitate. When it was washed the platino-potassic compound resembled the first one in all respects, although it contained the chloro-salt in a granular state. On desiccating it at 100° , in the covered platinum vessel, it became a very brilliant citron-yellow.

When put into a hydrogen flame *before being desiccated*, on a recently heated loop of pure platinum wire, it coloured it first of all *greenish blue*, and then *violet-blue*. Spectrum analysis of the flames showed, side by side with the potassium spectrum, which was identical with that of the first chloroplatinate, the sodium line more distinct than in hydrogen burning in the same atmosphere. Still, the sodium line was no more intense than in the first chloroplatinate.

After desiccation the chloro-salt was kept in a covered platinum dish, under the same bell-jar as the former.

The washings from the chloroplatinate were added to the filtrate; the total amount of liquid was about *two thousand six hundred c.c.* I concentrated it down to *seven hundred c.c.* in the platinum still. On cooling the liquid, a noticeable amount of chloroplatinate was deposited.

Whilst still leaving this compound in the liquid I added to it, *when cold*, little by little, and stirring it continuously, so much of a 10 per cent solution of platinic chloride as would cloud it, so as to eliminate from it all the metal capable of being thus precipitated in the form of chloroplatinate. After leaving it for eighteen hours at rest, I poured off the filtrate, which was very slightly coloured yellow, and washed it by decantation, just as I did with the two former chlorates. The washings had already dissolved more than a third of the volume of chloroplatinate, and, as I could still detect free platinic chloride in them after evaporation, I finished the washing with cold absolute alcohol.

After washing, the chloroplatinate was a citron-yellow, resembling the colour taken by the flocculent chloro-salt when heated to 100° , but without being so brilliant.

When moistened with alcohol and put once more into a hydrogen flame, in a recently heated loop of fine platinum wire, it gave it a greenish blue colour, which soon changed to violet-blue. Spectrum analysis of the flame showed, side by side with the characteristic potassium spectrum, the sodium line just as sharp as in the two former chloroplatinates.

I removed the alcohol from the chloro-salt, and kept it for several days under a bell-jar over sulphuric acid.

The filtrate, containing the excess of platinic chloride used, and the saturated washings from the chloroplatinate, which ought to contain the more soluble chloro-salt if the alkaline chloride used was not chemically homogeneous, were carefully and gradually evaporated in a covered platinum retort, the neck of which reached as far as possible into a flask. When the volume of liquid was reduced by at least three-quarters, and it had already deposited the greater part of the dissolved chloro-salt, I chilled it quickly, so as to make a fine powdery deposit from the chloroplatinate still left in solution.

I got it all from the retort by turning it into a covered platinum funnel, fitted with a fine platinum wire sieve. The new filtrate, containing the bulk of the chloroplatinate, was evaporated to saturation, by boiling in the retort. The chloro-salt, deposited by cooling the concentrated liquid, was added to that already in the platinum funnel, while the new filtrate was put into the platinum retort and evaporated to dryness on the water-bath. The residue, consisting of platinic chloride and chloroplatinate of potassium, was taken up by absolute alcohol, and the whole poured into the platinum funnel containing the chloroplatinate. I then dried the mass of chloro-salt by cold absolute alcohol. Having covered the funnel with a bell-jar, I continued to wash it with alcohol so long as I could detect the presence of platinic chloride in the washings.

Having introduced some chloroplatinate, dried with alcohol, by means of a recently heated loop of fine platinum wire into a hydrogen flame, I found that it coloured this flame greenish blue, changing to a violet-blue. Spectrum analysis of these flames, repeated several times, showed a *potassium spectrum* identical with that of the *three preceding chloroplatinates*, and the sodium line a little stronger than in these three chloro-salts.

Having found, by the addition of anhydrous ether, that chloroplatinate was present in the alcohol used to wash the chloroplatinate of potassium, I added anhydrous ether until the reaction ceased. To produce this effect, it required a quantity of ether equal to *two-thirds* of the volume of alcohol. The precipitate, when drained by a mixture of equal parts of ether and absolute alcohol, collected, and dried, weighed 0.0474 grm. from 2435 c.c. of etherised alcohol: when very carefully examined I found that the dull yellow precipitate was formed entirely

of chloroplatinate of potassium. In fact, until the alkaline metal it contained was entirely volatilised, it gave the potassium spectrum with the sodium line, in spite of the most careful way the chloroplatinate had been washed with alcohol only.

Wishing to ascertain the nature of the chloro-salt left with the platinic chloride in the etherised alcohol, I added to it, firstly, pure water, and then a solution of pure chloride of ammonium, in sufficient bulk to reduce the platinic chloride to chloroplatinate, and I gradually distilled the whole mass, in the platinum retort, first on a bath, and then on an open fire, so as to completely dry the residue.

I dissolved the residue in boiling water, and evaporated the solution in a *platinum boat*, on a bath, under a damp bell-jar. The chloroplatinate, which was a pale and dull yellow, was reduced in hydrogen at the lowest possible temperature, in the platinum boat in a combustion-tube. I then volatilised the chloride of ammonium produced, in hydrogen. In fact, the chloroplatinate of ammonium was divided in the hydrogen into platinum and chloride of ammonium, below the temperature at which this compound volatilises. The sal-ammoniac formed during the reaction re-forms in a powdery state on the surface of the metal reacted upon.

After the reaction, I put the grey platinum residue in the boat into pure water, and immediately evaporated it in another platinum boat, weighing all the filtered washings in a tube with a ground-glass stopper. The residue after evaporation, previously dried at 150° , was quite white. Its weight, determined by substitution, after cooling it in dry air, was about 0.01375 gm. This residue was highly hygroscopic, and had a *strong alkaline reaction*. I found, on spectroscopic examination, that it consisted entirely of *chloride of calcium, with traces only of sodium and potassium*.

Eighty grms. of chloride of potassium, entirely free from calcium and sodium, were experimented on. I made some platinic chloride from *one hundred and fifty grms.* of platinum prepared by Mr. Matthey, of London, and free from iron, iridium, rhodium, silicon, and sodium. *Eight litres* of pure water, condensed and collected on platinum, were used to dissolve and wash it.

After the numerous experiments I have made on water condensed by means of platinum refrigerators and aqua regia, I am in a position to state that the calcium found in the residue comes from neither the water nor the aqua regia. I must, then, suspect that there is at least a possibility that the calcium has been brought to the platinum, which was melted in a lime crucible, by the air in the glass cage, at the same time as the traces of sodium, in spite of the unremitting care I took to shelter it from atmospheric dust.

Besides, I have found on several occasions that, on remelting welded platinum in an oxyhydrogen blowpipe in the air, and then cooling* it in a lime crucible, the calcium spectrum is visible for several moments.

I reduced separately the chloroplatinate made first and last, and together that made second and third. These reductions were performed in a platinum retort in a magnesia bath, with the same arrangements and in the same manner that I described on pages 675 and 676 of my "New Researches on the Laws of Chemical Proportions," and taking special care to carry it out *at the lowest possible temperature*, so as not to lose the alkaline chloride liberated, and to continue the liberation of hydrogen at this temperature so long as this gas carries hydrochloric

acid with it. I then heated the magnesia bath in which the retort stood, until the mercury, in a tube stopped at one end, when slanted and put deep into the magnesia, began to boil gently. I kept the product of the reduction of chloroplatinate thus for *one hour* in a slow current of pure dry hydrogen, and I thus drove off the hydrochloric acid which was so obstinately held by the alkaline chloride. All the chloroplatinate used was reduced in three operations.

The mass was lixiviated in pure fresh water. The chloride of potassium solution, whether saturated or dilute, was *colourless*, which is never the case when the chloroplatinate is not wholly reduced. This solution, after being filtered through paper which had been washed in succession with dilute hydrofluoric and hydrochloric acids and with pure water, and being evaporated in platinum under a bell-jar, left a white saline residue, which, when melted in a covered platinum crucible, formed a liquid free from any trace of platinum in suspension. *This liquid, when poured into a platinum vessel, formed a clear and colourless button.*

A part of the three melted chlorides, when dissolved in water, made a perfectly *clear* solution, *neutral* to litmus paper and also to phenolphthalein. This solution coloured a hydrogen flame *violet-blue*. Spectrum analysis of the flame showed the sodium line in *all three chlorides*, as well as the potassium spectrum, and clearer than in the same hydrogen burning in air. As a check, I put into the flame some chloride made from the chlorate, used in preparing the chloroplatinate, and a comparison showed the same result.

I proved that the spectra of all *three* chlorides obtained from chloro-platinic salts were *identical*, and, *excepting for traces of the sodium line, that they were identical with the spectrum of the chloride used in preparing the chloroplatinates.*

The long and delicate work in which I was engaged, by using *large and costly platinum apparatus, which were generously lent to me*, thus confirmed the results of my previous researches on the homogeneity of potassic chloride made from chloroplatinate, and showed once more that I was not able to procure by this means a chloride which did not show the sodium line.

By the method described in a previous note I evaporated, successively, on a flat dish of pure platinum, *five grms.* of chloride made during the *first* and *last* reductions, and *ten grms.* of chloride from the chloroplatinates made during the *second* and *third* precipitations. These three masses of chloride were volatilised without leaving on the platinum dish a trace of residue visible under a microscope.

Excepting for minute traces of sodium brought by the platinic chloride, those three parts form the body which combines with platinic chloride, and their molecular affinity to silver ought to be the true affinity of this metal for chloride of potassium, regarded as a distinct substance, if, as is probable, if not certain, *owing to the identity of their spectra*, future experiments show that they are identical among themselves and with the chlorides from chlorate and perchlorate of potassium.

In a special article I shall describe the researches I undertook in order to throw light on these different questions.

(To be continued).

* Since the conclusion of these researches and the publication of this note, Mr. Matthey, of London, has sent me for examination a specimen of *very bright spongy* platinum, made by *volatilisation* during the process of completely fusing this metal on a large scale, in oxy-coal gas, in a lime crucible. This sponge, on exposure to damp air, is quickly dulled, by coating itself with hydrocarbonate of calcium. On separating the calcic hydrocarbonate by means of dilute hydrochloric acid, the residual platinum is quite dull and of a bluish grey tint. It is probable that the bright sponge, whiter than platinum, consists of an alloy of calcium and platinum.

Messrs. F. Wiggins and Sons, Mica Merchants, wish to notify that, owing to the great increase of business necessitating additional warehouse room, they have purchased No. 103, Minories, and that during the demolition and re-building of that and their old house, No. 102, Minories, they have taken temporary premises at Nos. 62 and 63, Minories (opposite), where for the next twelve months all communications should be addressed, or to their other establishment, 10, Tower Hill, London.

THE PREPARATION OF PERCHLORIC ACID AND ITS APPLICATION TO THE DETERMINATION OF POTASSIUM.*

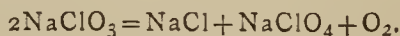
By D. ALBERT KREIDER.

VARIOUS methods for the preparation of perchloric acid have been developed through the long felt want of a process in which the elements of time and danger would be reduced to a minimum and the product increased to quantities commensurate with the growing use of the acid in analytical chemistry. Most of these methods have been found impracticable because of the incidental formation of the dangerously explosive oxides of chlorine, or the time required in refining the product from the impurities introduced with the reagents employed.

Doubtless the best process thus far offered is that of Caspari (*Zeitschr. für Ang. Chem.*, 1893, p. 68), which, however, is to an objectionable degree exacting of time and labour. The product has to be treated and re-treated for the removal of potassium and then for the extraction of the hydro-fluosilicic acid, and at several stages is for this purpose to be left standing for from 24 to 48 hours. Under the most favourable circumstances it could not be prepared in less than 5 or 6 days, and during a great many hours of that time it requires close attention.

The great difficulty has always been with the necessity of a perfect separation of potassium from the perchloric acid, which has been prepared by the ignition of the potassium chlorate. If, for the manufacture of the perchlorate, the chlorate of sodium—which, if not upon the shelves of every laboratory, is nevertheless in the market, almost, if not entirely free of potassium—be used instead of the potassium salt, the complete removal of the base will be unessential; since its presence in the determination of potassium will exert no influence other than that which is beneficial. It is well known that because of its deliquescence and the almost equal solubility of sodium perchlorate with that of the chloride, its separation from the latter by re-crystallisation from an aqueous solution, as in the case of potassium, is impossible. But the insolubility of the chloride of sodium in strong hydrochloric acid, with the aid of the acid-proof Gooch crucible, affords a means for the liberation of the perchloric acid and the removal of the greater part of the sodium in one operation. Upon this basis, therefore, the following simple method was elaborated.

A convenient quantity of sodium chlorate, from 100 to 300 grms., is melted in a glass retort or round-bottomed flask and gradually raised to a temperature at which oxygen is freely, but not too rapidly, evolved, and kept at this temperature till the fused mass thickens throughout, which indicates the complete conversion of the chlorate to the chloride and perchlorate, and requires between one and one-half to two hours; or the retort may be connected with a gasometer and the end of the reaction determined by the volume of oxygen expelled, according to the equation—



The product thus obtained is washed from the retort to a capacious evaporating dish, where it is treated with sufficient hydrochloric acid to effect the complete reduction of the residual chlorate, which, if the ignition has been carefully conducted with well distributed heat, will be present in but small amount. It is then evaporated to dryness on the steam bath, or more quickly over a direct flame, and with but little attention until a point near to dryness has been reached, when stirring will be found of great advantage in facilitating the volatilisation of the remaining liquid and in breaking up the mass of salt. Otherwise the perchlorate seems to solidify with a certain amount of water, and removal from the dish, without moistening and re-heating, is impossible.

After triturating the residue, easily accomplished in a porcelain mortar, an excess of the strongest hydrochloric acid is added to the dry salt, preferably in a tall beaker, where there is less surface for the escape of hydrochloric acid, and from which the acid can be decanted without disturbing the precipitated chloride. If the salt has been reduced to a very fine powder, by stirring energetically for a minute, the hydrochloric acid will set free the perchloric acid and precipitate the sodium as chloride, which in a few minutes settles, leaving a clear solution of the perchloric acid with the excess of hydrochloric acid. The clear supernatant liquid is then decanted upon a Gooch filter, through which it may be rapidly drawn with the aid of suction, and the residue re-treated with the strongest hydrochloric acid, settled and again decanted, the salt being finally brought upon the filter, where it is washed with a little strong hydrochloric acid. A large platinum cone will be found more convenient than the crucible, because of its greater capacity and filtering surface. When the filter will not hold all the sodium chloride, the latter after being washed may be removed by water or by mechanical means, with precautions not to disturb the felt, which is then ready for the remainder. Of course, if water is used, the felt had better be washed with a little strong hydrochloric acid before receiving another portion of the salt. This residue will be found to contain only an inconsiderable amount of perchlorate, when tested by first heating to expel the free acid and then treating the dry and powdered residue with 97 per cent. alcohol, which dissolves the perchlorate of sodium, but has little soluble effect on the chloride.

The filtrate containing the perchloric acid with the excess of hydrochloric acid and the small per cent of sodium chloride which is soluble in the latter, is then evaporated over the steam bath till all hydrochloric acid is expelled and the heavy white fumes of perchloric acid appear, when it is ready for use in potassium determinations. Evidently the acid will not be chemically pure because the sodium chloride is not absolutely insoluble in hydrochloric acid; but a portion tested with silver nitrate will prove that the sodium, together with any other bases which may have gone through the filter, has been completely converted into perchlorate, and unless the original chlorate contained some potassium or on evaporation the acid was exposed to the fumes of ammonia, the residue of the evaporation of a portion is easily and completely soluble in 97 per cent alcohol, and its presence is therefore unobjectionable. One c.c. of the acid thus obtained gave on evaporation a residue of only 0.036 gm., which was completely soluble in 97 per cent alcohol.

Caspari's acid under similar treatment gave a residue in one case of 0.024 gm. and in another 0.047 gm. If, however, a portion of pure acid be required, it may be obtained by distilling this product under diminished pressure, and, as Caspari has shown, without great loss providing the heat is regulated according to the fumes in the distilling flask.

Some modification of the above treatment will be found necessary in case the sodium chlorate contains any potassium as an impurity, or if the latter has been introduced from the vessel in which the fusion was made. Under these circumstances the hydrochloric acid would not suffice for the removal of potassium, since a trace might also go over with the sodium, and thus on evaporation a residue insoluble in 97 per cent alcohol be obtained. To avoid this difficulty, the mixture of sodium perchlorate and chloride, after being treated with hydrochloric acid for the reduction of the residual chlorate, being reduced to a fine powder, was well digested with 97 per cent alcohol, which dissolves the sodium perchlorate but leaves the chloride as well as any potassium salt insoluble. By giving the alcohol time to become saturated, which was facilitated by stirring, it was found on filtering and evaporating that an average of about 0.2 gm. of sodium perchlorate was obtained for every c.c. of alcohol, and that

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xlix., June, 1895.

the product thus obtained was comparatively free of chlorides, until the perchlorate was nearly all removed, when more of the chloride seems to dissolve. This treatment with alcohol is continued until, on evaporation of a small portion of the latest filtrate, only a small residue is found. The alcoholic solution of the perchlorate is then distilled from a large flask until the perchlorate begins to crystallise, when the heat is removed and the contents quickly emptied into an evaporating dish, the same liquid being used to wash out the remaining portions of the salt. When the distillation is terminated at the point indicated, the distillate will contain most of the alcohol employed, but in a somewhat stronger solution, so that it requires only diluting to 97 per cent to fit it for use in future preparations. The salt is then evaporated to dryness on the steam bath and subsequently treated with strong hydrochloric acid for the separation of the perchloric acid.

One c.c. of the acid prepared in this way on evaporation gave a residue in one case of 0.0369 grm., and in another 0.0307 grm., completely soluble in 97 per cent alcohol, which was then ignited and the chlorine determined by silver, from which the equivalent of perchloric acid in the form of salts was calculated as 0.0305 grm. By neutralising the acid with sodium carbonate, evaporating, igniting in an atmosphere of carbon dioxide till decomposition was complete, collecting the oxygen over caustic potash, allowing it to act on hydriodic acid by intervention of nitric oxide, according to a process soon to be published, titrating the iodine liberated, with standard arsenic and calculating the equivalent of perchloric acid, after subtracting the amount of acid found in the form of salts, the amount of free acid per c.c. proved to be 0.0831 grm.

The whole process, even when the separation with alcohol is necessary, can not well require more than two days, and during the greater part of that time the work proceeds without attention.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 5th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from vol. lxxii., p. 316).

148. "Derivatives of α -Hydrindone." By C. REVIS and F. STANLEY KIPPING, Ph.D., D.Sc.

The study of α -hydrindone (*Trans.*, 1894, 480) has been continued, and attempts have been made to convert it into $\alpha\beta$ -diketohydrindone; up to the present, however, this substance has not been obtained.

Two compounds are formed on treating α -hydrindone with a solution of bromine in soda according to the conditions of the experiment; if the ketone be simply shaken with the alkaline solution at ordinary temperatures, it is slowly converted into a bulky mass consisting of ordinary dibromohydrindone (m. p. 132°), whereas if the mixture be heated on the water-bath a heavy crystalline powder is formed, apparently by further action on the dibrom-compound. The latter is very sparingly soluble in most ordinary solvents, but may be crystallised from boiling acetic acid, from which it separates in long colourless needles decomposing between 250° and 260°. Analyses show it to be a condensation product of the composition $C_{18}H_{12}O_3$, but its constitution has not yet been established.

When monobromohydrindone is dissolved in alcoholic potash at ordinary temperatures it furnishes a substance which crystallises from chloroform in large, transparent,

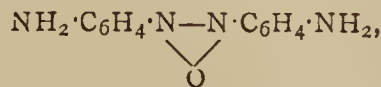
well-defined prisms. This compound is a condensation product of the composition $C_{18}H_{12}BrO_2$.

Dibromohydrindone (m. p. 132°) is readily acted on by alcoholic potash yielding various products according to the conditions of the experiment.

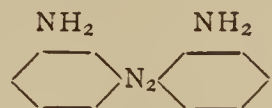
If the potash be added gradually until the solution becomes permanently alkaline, the dibromo-derivative is converted into a new substance, which crystallises from benzene in lustrous needles of indefinite melting-point (decomposing from 150° to 160°).

149. "The Alkaline Reduction of Metanitriline." By RAPHAEL MELDOLA and ERNEST R. ANDREWS.

On heating an aqueous solution of metanitriline with alkaline reducing agents, such as sodium stannite, the azoxy-compound,—



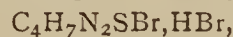
scales (from toluene) or needles (from boiling water or dilute alcohol); m. p. 146–148°. The diacetyl-derivative (m. p. 254°), the disazimide (m. p. 86–85°), the disazo- β -naphthol derivative (m. p. 244–245°), and the metadiiodo-azoxybenzene (m. p. 118–119°), have been prepared from the diamidoazoxy-compound. The corresponding azo-compound, having the constitution—



has been prepared by the complete reduction of the azoxy-compound to a hydrazo-compound by the action of zinc-dust and alkali, and subsequent re-oxidation. This has been found the most effective way of obtaining the azo-compound in a state of purity. It consists of dull orange needles when crystallised from boiling water; m. p. 150–151°. The diacetyl-derivative (m. p. 272°), the dibenzoyl-derivative (m. p. 284–285°), the disazo- β -naphthol (m. p. 282°), and the oxalate of the base have prepared, and are described in the paper. The constitution was confirmed by conversion into the metadiiodoazobenzene (m. p. 150–151°) of Gabriel (*Ber.*, 1876, ix., 1410). Both the azoxy- and azo-compounds are well-characterised bases forming diacid salts. The paper concludes with a theoretical discussion by one of the authors (Meldola) of the process of reduction of nitro-compounds.

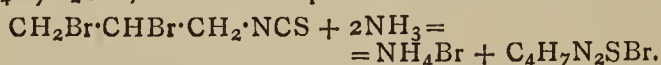
150. "The Chemistry of Dibromopropylthiocarbimide; and the Action of Bromine and Iodine upon Allylthiourea." By AUGUSTUS E. DIXON, M.D.

Having failed to obtain dibromopropylthiourea from $\beta\gamma$ -dibromopropylthiocarbimide and ammonia (*Trans.*, 1892, lxi., 548), the author proceeded to re-examine a compound obtained by Maly (*Zeits. f. Chem.*, 1867, 42) from allylthiourea and bromine. This compound, "thiosinamine dibromide," $C_4H_8N_2SBr_2$, is, however, not dibromopropylthiourea, but proves to be the hydrobromide of a well-marked base, $C_4H_7N_2SBr$, which is precipitated, on the addition of caustic alkali, as a dense, almost colourless, strongly alkaline oil. The oil is sparingly soluble in water; it combines with hydrochloric acid to form the hydrochloride, $C_4H_7N_2SBr \cdot HCl$, hard white prisms melting at 129–130°, and identical with the "bromochloride" obtained by Maly from "thiosinamine dibromide" and moist $AgCl$. The hydrobromide,—

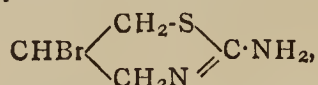


from the base and HBr , is identical with the dibromide; it was found to melt at 139–140°. By treatment of either the free base or its hydrobromide with picric acid, the salt $C_4H_7N_2SBr \cdot C_6H_2(NO_2)_3OH$ is precipitated; when re-crystallised from dilute spirit it forms minute, glittering prisms, pale yellow in colour, and melting at 187–188°. Heat is evolved on mixing dibromopropylthiocarbimide

with alcoholic ammonia; ammonium bromide separates, and is left, together with a brownish syrup, when the alcohol is evaporated: this syrup is the brominated base $C_4H_7N_2SBr$, somewhat impure.

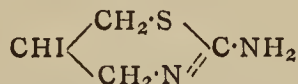


Reasoning from the conditions under which the base is produced, from its alkaline character, and from the fact that it is not desulphurised by treatment with alkaline lead, or ammoniacal silver solutions, the author regards it as having the probable constitution—



i.e., μ -amido- γ -brompenthiazoline, otherwise β bromotrimethylene- ψ n-thiourea. This view also receives support from the results of experiments by Gabriel and others, on the interaction of brominated fatty bases with thiocarbimides, whereby the tendency has been shown of monohalogenised fatty thioureas to lose, at the moment of formation, their contained halogen, with production of the corresponding haloïd salts of closed-chain bases of the above type.

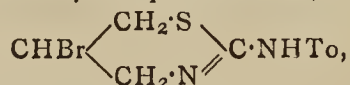
Iodine appears not to combine with allylthiocarbamide, but acts similarly to bromine on allylthiourea, giving the hydriodide of an iodised base, $C_4H_7N_2SI, HI$. The salt is freely soluble in water or spirit, and melts at $132.5-133.5^\circ$. When treated with caustic potash the base is thrown down as a dense, sticky oil, alkaline to litmus, nearly insoluble in water, reacting (like its brominated analogue) for halogen with chlorine water, and yielding a picrate of m. p. $176-177^\circ$. The constitution assigned to it is—



= μ -amido- γ -iodpenthiazoline.

Similar compounds were obtained by acting with organic bases upon dibromopropylthiocarbimide.

μ -Orthotolylamido- γ -brompenthiazoline,—

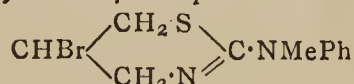


from the thiocarbimide and *o*-toluidine, was deposited from alcohol in rhombic plates, m. p. $134.5-135.5^\circ$. It is insoluble in water, rather difficultly soluble in alcohol, feebly alkaline to litmus, and—like the other compounds of its class—retains its sulphur, even when boiled with alkaline lead, or ammoniacal silver salts. The hydrobromide is a clear, pale brown, apparently uncrystallisable, acid syrup.

μ -Paratolylamido- γ -brompenthiazoline hydrobromide, formed a thick, acid syrup; the free base occurred in rosettes of pointed white prisms melting at $124-125^\circ$.

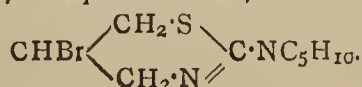
$\mu\alpha$ -Naphthylamido- γ -brompenthiazoline, like its hydrobromide, could only be obtained as a liquid. The hydrobromide of the corresponding β -naphthyl-compound was a brownish, tenacious acid syrup; its base occurred in brilliant prisms, neutral at litmus, and melting at $190-191^\circ$.

μ -Methylphenylamido- γ -brompenthiazoline,—



(from the thiocarbimide and methylaniline, with evolution of heat), separated as a colourless oil; its hydrobromide is crystalline, easily soluble in hot water, and melts at $183-184^\circ$.

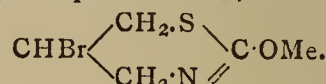
μ -Piperidyl- γ -brompenthiazoline,—



Produced with evolution of heat; the HBr salt forms colourless, vitreous prisms, soluble in cold water, with neutral reaction; m. p., $189-190^\circ$. The base is a nearly colourless syrup, which does not afford bromine when mixed with chlorine water: it is so strongly alkaline as to allow of titration by standard acid.

By acting with methylic, ethylic, and propylic alcohols respectively at a little over 100° on the thiocarbimide, the three following compounds were obtained, together with (free) hydrogen bromide.

μ -Methoxy- γ -brompenthiazoline,—

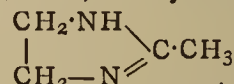


White crystals easily soluble in hot water; not desulphurised by silver or lead salts; m. p., $95-96^\circ$. The silver compound becomes purple on short exposure to actinic light.

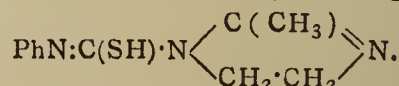
μ -Ethoxy- γ -brompenthiazoline.—Small white prisms, moderately soluble in hot water; m. p., $96-97^\circ$. Forms a silver compound which is very markedly light-sensitive.

μ -Propoxy- γ -brompenthiazoline.—Pyramidal crystals; m. p., $96-97^\circ$; closely resembling the preceding compound in properties.

Phenyl and orthotolylthiocarbimides respectively combine, evolving heat, with μ -methylimidazoline,—



(ethenylethylene diamine), thereby affording—



μ -Methylimidazolylphenylthiourea.—Thick, lustrous prisms, difficultly soluble in cold water or alcohol; desulphurised by lead and silver salts; m. p., $173-174^\circ$.

μ -Methylimidazolyl-*o*-tolylthiourea.—White crystals, melting at $159-159.5^\circ$, and generally resembling the corresponding phenyl-derivatives.

Helmholtz Memorial Lecture.

The Helmholtz Memorial Lecture will be delivered by Professor G. F. Fitzgerald, F.R.S., at an extra meeting of the Society to be held on Thursday, January 23, 1896, at 8 p.m.

NOTICES OF BOOKS.

Service Chemistry: being a Short Manual of Chemistry and its Applications in the Military and Naval Services. By VIVIAN B. LEWES, F.I.C., F.C.S., Professor of Chemistry, Royal Naval College, Greenwich; Associate of the Institution of Naval Architects, &c. Second and Revised Edition, Illustrated. 8vo., pp. 558. London: W. B. Whittingham and Co., Limited, Gracechurch Street, E.C.

THE author of this text-book does not fail to remind his readers that there is but substantially one chemistry, alike for the military and naval officer, for the metallurgist, the medical man, the agriculturist, or the dyer, and that its special adaptation to any one subject is merely an expansion of this one Science in some given direction. Few of the applications of our Science, indeed, are so manifold as those involved in the military and naval arts. They include the doctrine of explosives, the properties of metals and their alloys, as manifested in ordnance, in the sheathing and armour coating of ships, and sanitary chemistry in the most varied sense of the term. It is perhaps fortunate that no one class of experts is

responsible for all these departments. Thus the medical officer—if in these days he is duly listened to—is, or should be, alone entitled to decide on the fitness of a drinking water supply, whether on ship-board or for troops on the march. At the same time the tendency of any water to form "crock," or to corrode boiler plates, is on the home-stations committed to a technical chemist, and during long voyages may fall into the hands of the chief engineer.

After a clear, but necessarily brief, exposition of the fundamental principles of chemistry, we find an account of electrolysis, with especial reference to the mutual relations between different metals on ships' bottoms, and to the arguments for and against the use of zinc protectors. Three important chapters are given to the properties and purification of waters. The filtering material which is found most satisfactory is "cabalite," the composition of which is not stated.

There is no mention of Pasteur's (Chamberland's) filter, which, though probably the most efficient known, is too slow in its action for supplying a ship's company, and would be too cumbrous for troops on the march. The peril of drinking unfiltered water in tropical countries is great, since it may contain the germs of the *Filaria*. Even in temperate and cold climates it may serve as a medium for the introduction of hydatidous disease, which is always a possible contingency in any water to which dogs have access, alike in chilly Iceland and in hot Queensland. It is not generally known that in times of drought, in the latter country, the shepherds and stockmen will drink from a water-hole in which a sheep or a bullock is putrefying, whilst they utterly avoid one containing the remains of a dog.

It is to be hoped that due provision has been made for ensuring a safe water-supply for our troops on the Ashanti expedition. In the last Ashanti war the addition to the water of a mixture of alum, clay, and charcoal, as recommended by Mr. Crookes, was found very serviceable.

As a matter of course explosives receive prominent attention in the work before us. The number of such compounds and mixtures is now excessive, though but few of them are likely to be of practical importance. Melinite—the much-extolled French explosive—has been, the author considers, over-rated. If it was used in the late Madagascar war, no phenomena are recorded which could be traced to its action. Its main ingredient is picric acid. This acid has been repeatedly patented in different mixtures, and it has been officially experimented with both in Britain and Germany. The "smokeless powder" adopted in the British services—cordite—is a mixture of 58 per cent nitroglycerin, 37 per cent trinitro-cellulose, and 5 per cent of vaselin. It is made at the Government works at Waltham Abbey, and evidently requires great care and skill in its manufacture and storage, as several accidents have occurred at the works. It is found, as the author tells us, to withstand the cold of a Canadian winter, or the heat of an Indian summer, without accident or detriment. He recommends that on board ship it should be kept in water-jacketed magazines. No complaints of inconvenience from its combustion-products have been raised either from the army or the navy.

Accidents from "fire-damp" might seem to be outside the scope of Service Chemistry. But, unfortunately, explosive gaseous mixtures may be generated in the coal-bunks of a large steamer, and the same precautions are required as in a coal-mine. Safety lamps are requisite if the coal requires to be moved.

The storage of coal in a wet or broken state may lead to spontaneous combustion. A careful inquiry has been made by Government as to the kinds of coal required for service purposes, and the conclusion comes to is that a mixture of two-thirds Welsh and one-third North-country coal is recommended for use in the Navy.

This work will commend itself to the use of the authorities in both Services.

Direct Spectral Analysis of Minerals. (Analyse Spectrale Directe des Minéraux). By M. ARNAUD DE GRAMONT, Doctor in Science. 8vo., pp. 207. Paris and Liege: Baudry and Co. 1895.

IN this little work M. de Gramont suggests and explains a novel method for the spectroscopic examination of minerals. He has observed that many minerals possessing a metallic lustre, such as galena and pyrites, are such good conductors that an electric spark may easily be caused to pass over between their fragments. He has therefore undertaken to study if the spectroscopic examination of such sparks may not furnish a new method for a direct qualitative examination of the elements present in the minerals in question.

After describing the appliances necessary—far from complicated—the author remarks that minerals which are electro-conductive, or even which are only volatilised in the spark, behave spectroscopically like alloys, though like alloys in which the non-metals also give line-spectra like the metals. It is only needful to take into consideration certain rays of the air which persist among those of the elements of the mineral, and which are found laid down in a table.

M. de Gramont's researches lead him to the opinion that this method of examination will be serviceable in mineralogy, metallurgy, and in qualitative analysis, and will often indicate the presence of substances occurring in quantities so small as not to be detected by the wet way.

The work before us gives a description of the apparatus for producing the spark, and then that of the dispersive apparatus used in its spectral analysis.

It then gives an account of the behaviour of each of the elements under the conditions experimentally ascertained.

The tables of the wave-lengths of the minerals studied are very elaborate, and will prove extremely useful in research.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 24, December 9, 1895.

M. Marey's Official Visit to the Royal Society.—M. Marey, in his character as President of the Academy of Sciences, was present at the Anniversary Meetings of the Royal Society. In giving an account of his mission he refers to the expressions of esteem and friendship for the *savants* of France which were uttered by the retiring President, Lord Kelvin, and by his successor designate, Sir J. Lister. The main subject of the meetings was the proposed creation of a grand international catalogue of all the works published in the entire world on all branches of Science. It is well known that the Royal Society has already published a catalogue showing under the name of each author a list of all his writings from the year 1800 downwards. But such a catalogue fails to indicate the researches published on any given subject. To fill up this deficiency the Royal Society proposes to address all Governments through diplomatic channels, to appoint delegates to an international conference to agree on the best means of carrying out this project.

Analysis of Aluminium and its Alloys.—Henri Moissan.—This paper will be inserted in full.

Appreciation of Flours for Baking Purposes. Determination of Remnants of Bran and Germ which may Diminish the Yield of Bread.—Aimé Girard.—This paper also will appear at some length.

Analysis of Soils by Plants.—G. Lechartier.—This paper also will be inserted in full.

Absorption of Nitrogen by Cold Lithium.—H. Deslandres.—M. Gantz has announced recently (*Comptes Rendus*, 1895, p. 777) that lithium prepared by his method absorbs nitrogen rapidly and even with incandescence at temperatures below dull redness. I am indebted to the courtesy of M. Berthelot for some fragments of this lithium, and I have repeated this experiment with atmospheric nitrogen for the preparation of argon, and with the gas from the springs of Maizières (Côte d'Or) to effect its spectroscopic analysis, at the request of M. Moureu. But I observed at the same time a notable escape of hydrogen; therefore to eliminate this gas I was obliged first to heat the lithium in a vacuum for some hours at a temperature below the softening point of ordinary glass. The lithium scarcely melts, and its surface, which is covered with a dull blackish layer, splits up and shows at many points the brilliant metal. At the same time a metallic specular deposit is formed on the cold sides of the glass. If we then introduce the nitrogen, the tube being well cooled and no heat being applied, we observe a slow absorption of the gas in the cold analogous to the slow absorption of oxygen by phosphorus in the cold. The absorption is complete, for the spectral bands characteristic of nitrogen disappear absolutely. The dull blackish layer above mentioned is formed on contact with the air. If we cut a piece of lithium the freshly cut surfaces are brilliant like those of sodium, but tarnish rapidly. Now this dull blackish layer appears to be an obstacle to the action of nitrogen and lithium. As long as it is continuous, without fissures, no absorption takes place. On the contrary, the absorption is the more rapid the larger the surface of the lithium laid bare at the commencement of the experiment. I thought it useful to mention this property of lithium since we do not yet know any substance which absorbs nitrogen alone in the cold.

Possible Process for the Separation of Argon and Atmospheric Nitrogen.—Claudius Linb.—Will be inserted in full.

Action of Alcohol upon Mercurous Iodide.—Maurice François.—Boiling alcohol decomposes mercurous iodide. The decomposition ceases when 100 grs. of the liquid contain in round numbers 0.220 grm. of mercuric iodide in solution. This reaction is reversible, and the inverse action stops at the same limit. The quantitative separation of mercuric and mercurous iodides by means of alcohol is not exact.

New Synthesis of Pararosaniline and its Mono-, Di-, Tri-, and Tetra-Alkylated Derivatives.—Maurice Prud'homme.—The limited reduction of nitrobenzene gives rise to phenylhydroxylamine, which mineral acids convert into para-amidophenol (the reciprocal transformation of the hydroxyl of the radicle NH.OH and of the hydrogen in the para-position next to this radicle. The shade of the series of rosanilines becomes gradually more violet as the number of alcoholic radicles in the amidogenic groups is increased.

Mode of Decomposition of some Organic Bodies of Amidic and Imidic Functions.—Oechsner de Coninck.—The author has extended the method of Leconte and Yvon to the amides and imides of the fatty and of the aromatic series.

Limits of Approximation given by the "Grisometer" with a Platinum or Palladium Wire for the Determination of Formene Gas.—J. Coquillion.—This paper is not suited for useful abstraction.

Distribution of Boric Acid in Nature.—H. Jay.—Boric acid is distributed over the chief part if not over the entire globe. Plants, whether cultivated or wild, absorb from the soil and the water any boric acid which they meet with. Boric acid if introduced in small doses into the stomach of animals, is not assimilated, but is eliminated in the urine and other excretions.

Solubility and Activity of Soluble Ferments in Alcoholic Liquids.—A. Dastre.—The proteolytic ferment trypsin is soluble in alcoholic liquids of percentages up to 55°. The solubility is well marked at from 10 to 25 per cent, and then diminishes rapidly up to 50 per cent. The amylolytic ferment is still more soluble. Its solubility follows an analogous course to that of the foregoing, but extends up to 65 per cent. The ferments of the blood are sparingly soluble in alcoholic liquids, and cannot be recognised with solutions at 4 or 5 per cent.

MEETINGS FOR THE WEEK.

- MONDAY, 6th.—Society of Chemical Industry, 8. "A Technological Study of Comparative Affinities in the case of certain Salts of Ammonia," by Watson Smith, F.C.S. "Colour Effect of Lime Salts on Hops in Brewing," by J. W. Lovibond.
- TUESDAY, 7th.—Royal Institution, 3. (The Christmas Lectures). "Sound, Hearing, and Speech," by Prof. J. G. McKendrick, M.D., F.R.S.
- WEDNESDAY, 8th.—Society of Public Analysts, 5. (Annual Meeting). "Determination of Oxygen in Commercial Copper," by Bertram Blount. "Note on a Series of Analyses of a Private Water Supply," by E. Russell Budden. "Note on the presence of Petroleum Oil in a Sample of Whisky," by W. F. Lowe.
- THURSDAY, 9th.—Royal Institution, 3. "Sound, Hearing, and Speech," by Prof. J. G. McKendrick, F.R.S.
- FRIDAY, 10th.—Astronomical, 8.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1885.

ON THE SOLUBILITY OF SILICA.

By Prof. ARTHUR M. EDWARDS, M.D., Newark, N.J.

I HAVE been considerably puzzled to find out just what was known respecting the solubility of silica, especially as it comes into my work just now. I am engaged in examining the soundings brought home by the U.S.S. *Tuscarora* made during the seasons of 1873 and 1874. They were placed in my hands by the Academy of Natural Sciences of California to report, where, at San Francisco, Cal., they were left by Commander George E. Belknap. The steamer crossed the Pacific Ocean several times, from the United States to Japan, and made soundings, one of which was in 4655 fathoms, the deepest that has been gotten. They were often in the "red clay" era of Professor Wyville Thomson, and sometimes in the "diatom ooze" of the same gentleman, taken during the celebrated voyage of H.M.S. *Challenger*. In fact, they crossed the line of the *Challenger*, and some of them are the same soundings as brought home by Captain Nares. What I got upon the solubility of silica were the following. Roscoe and Schorlemmer, in their "Treatise on Chemistry," vol. i., p. 566, say that there is only one oxide of silicon, the silicon dioxide or silica, SiO_2 . "It is found not only in the mineral, but in the vegetable and animal kingdoms, existing in large quantities in the glassy straw of the cereals and of bamboos, in the scales of the diatomaceæ, and in the feathers of certain birds, which have been found to contain as much as 40 per cent of this substance. The minute and beautifully formed spicules of the spongiidæ and radiolariæ also consist of pure silica."

"These are the organisms, the diatomaceæ (now known as the bacillariaceæ), the spongiidæ, and the radiolariæ, which I have to deal with, and I think there is not enough known of the chemistry of their shells. I will endeavour to make plain what I have discovered after over 40 years studying them. Silica, or quartz, occurs in three states. As quartz it crystallises in combinations of the hexagonal prism with the rhombohedron, with a specific gravity of 2.6 and a hardness of 7. It is colourless or slightly coloured by iron, manganese, or organic matter commonly."

The second form is tridymite. It crystallises like quartz in the hexagonal system, and is found in the trachytic porphyry at Pachuca, in Mexico. It has a specific gravity of 2.3, and hardness of 7.

The third form is amorphous silica, and occurs in nature not as a crystalline mass, but as opal. It is colourless, or variously coloured; specific gravity of 2.3. And not unfrequently crystals of tridymite are found in the non-transparent portions of opal. Chalcedony, agate, and flint are the common varieties. It has a specific gravity of 2.2 when melted, as it can be by the oxy-hydrogen flame.

"In all three conditions silica is insoluble in water, and also in all acids except hydrofluoric, in which it readily dissolves. Silica, however, is easily soluble in all alkalis, even in ammonia, and the more easily the finer its state of division. The amorphous variety, especially if it contains water, also dissolves in alkaline carbonates of the hot Islandic springs, which, on exposure to air, deposit this substance, the alkaline silicates being decomposed by the atmospheric carbonic acid, while silica and an alkaline carbonate are formed. The occurrence of silica in these springs was observed as long ago as 1794 by Black, but even before that date Bergman had shown that small quantities of silica were contained in solution in the water of many springs."

Professor Hilgard has shown that silica is present in the waters of the springs of California, without saying in what form it is present, only as silica. And this is the statement of writers generally. "Stannic acids" are generally held responsible as the dissolving matter. But I think I will show that the shells of bacillariaceæ are not always silica, and that they are soluble in rain water, which is not pure water.

The rain falls as pure water, but it comes into contact with the air, which is a mixture, not a compound, of nitrogen, oxygen, and argon, with various other substances, as carbonic anhydride, sulphur, and so forth. It therefore changes to an impure solution of air, oxygen, argon oxide (?), carbonic acid, and other things, but mostly ammonia. This was demonstrated by Schönbein over 30 years ago as a means by which the nitrogen goes to the plant life and afterward to the animal life of the globe.

Now ammonia in solution can dissolve silica which it finds in the soil, introduced there by the disintegration of the rocks. Silica is common in nearly all the rocks. It is pulverised very finely and just in the state to dissolve in alkaline (ammonia) solution. Silica pulverised and silica in the form of the shells of bacillariaceæ can be very readily dissolved in rain water, and also in all kinds of potable water. We have only to place some infusorial earth, which is the shells of bacillariaceæ, on a filter and pass potable water through it to find it dissolves very readily.

But the shells of bacillariaceæ are not always composed of silica. They may most commonly be composed of amorphous silica, most readily soluble in spring water. But they are commonly, as is seen in lacustrine sedimentary deposits, made up of clay, aluminium silicate, also readily soluble. They may sometimes consist of iron silicate, and most commonly of all the bacillariaceæ do not secrete all silica or a silicate at all, but their shells are made up of a compound resembling cellulose.

This I have found out by washing the shells in filtered spring water to see if I can wash them clean and mount them on a slide to make microscopic objects. I have found, to my sorrow, that they readily dissolve in fresh spring water, and I thought that the solubility of silica in water must be known to account for its presence in the soil, in spring water, and in the fossils of the earth.

I wish this communication to pass as a statement of the solubility of the shells of bacillariaceæ, and spongiidæ, and radiolariæ which are present in the infusorial earths and soundings.

HELIUM AND THE GAS X (?).

By R. M. DEELEY.

THE fact that three such experienced spectroscopists as Professors Runge and Paschen, and Mr. Norman Lockyer, should maintain that what has hitherto been regarded as helium is really a mixture of at least two elemental gases, should not be lightly passed over, even though the evidence may not be regarded as very satisfactory.

The reference made to this possibility in my short communication to the CHEMICAL NEWS of December 20th last, *might* be regarded as an indication that I considered that there is no place in the periodic system for another element of small atomic weight. Upon such a point the periodic law does not throw much light; for although the elemental gas X may exist it could not have been predicted.

Periodic tables, among which may be included Mendeleeff's, are generally so drawn up that if we were to regard each of their unoccupied spaces as indicating the existence of an unknown element, we should be compelled to regard our list of elementary substances as being still very incomplete. Some are satisfied that many of these spaces do not necessarily indicate that elements

TABLE I.

X	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	H
He	Li	Be	—	—	—	—	—	—	—	—	—	—	B	C	N	O	F
A	Na	Mg	—	—	—	—	—	—	—	—	—	—	Al	Si	P	S	Cl
—	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
—	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
—	Cs	Ba	La	Ce	Di	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	Yb	Ta	W	—	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
—	—	—	—	Th	U	—	—	—	—	—	—	—	—	—	—	—	—

TABLE II.

X	H	He	Li	Be	B	C	N	O	F	A	Na	Mg	Al	Si	P	S	Cl
?	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
?	Rb	Sr	Y	Zr	Nb	Mo	?	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
?	Cs	Ba	La	Ce	Di	?	?	?	?	?	?	?	?	?	?	?	?
?	?	?	Yb	?	Ta	W	?	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	?	?
?	?	?	?	Th	?	U	?	?	?	?	?	?	?	?	?	?	?

remain to be found for them, whilst others get out of the difficulty by asserting that such elements do exist, but say that they are never likely to be found.

In arranging the elements in tabular form I have endeavoured, whilst following the periodic theory of classification implicitly, to leave as few blanks as possible. I should, however, like to point out that, without doing any violence to Tables I and II (CHEMICAL NEWS, p. 297, December 20th, 1895), room can be found in the periodic system for at least one more element of small atomic weight. The altered arrangement is given in the accompanying tables.

In Table I. He is placed before Li, A before Na, and the new gas X at the commencement of the line at the extreme end of which is H. In Table II. X is the only element of the first column, and has an atomic weight less than that of H. This gives some support to the contention that there are spaces for elements between Cl and K, Br and Rb, &c.; but places such elements among the alkali metals instead of among the odd series elements. It also agrees with the reasoning of Professors Runge and Paschen, who state that the hypothetical gas X probably has a smaller atomic weight than helium. They also regard its spectrum as placing it among the alkali metals.

Making the order—

H	X	He	Li
?	K	Ca	Sc
?	Rb	Sr	Y

does not appear to be quite so satisfactory.

ON THE WAVE LENGTH OF THE D_3 HELIUM LINE.*

By A. DEFOREST PALMER, JR.

OWING to the recent increased interest in the wave length of the helium lines due to the discovery of terrestrial helium, I have been led to calculate some observations on the D_3 chromosphere line carried out by myself at the Physical Laboratory of the Johns Hopkins University during February and March, 1893.

The measurements were made on the large fixed telescope spectrometer used by Dr. Louis Bell (*Amer. Journ. of Science*, vol. xxxv., p. 265) in his determination of the absolute wave length of the D solar lines, with a plane speculum metal grating having about fourteen thousand lines to the inch and five inches of grating space. The telescopes of this instrument are 16.4 c.m. clear aperture and about 2.5 metres focal length; and with the grating used I obtained good dispersion and excellent definition in the first spectrum to the right of the normal to the

grating. All the observations were made in this spectrum on account of its superior definition.

An image of the sun about 1 c.m. in diameter was formed on the slit of the instrument by aid of a large Foucault heliostat, and an achromatic lens of about four inches aperture. Appliances were provided for moving the image laterally across the slit, and, by means of a total reflecting prism, for turning it about the direction of the beam as an axis to bring any desired point of the limb over the slit.

The D_3 line appeared only when the sun's image was tangent to the slit, and then as a bright but very short line in the centre of the field of view vertically considered. Its definition and intensity were found to vary greatly from day to day, and for different points on the sun's limb. In general, when a solar prominence lay across the slit the line was very broad and intense, but the definition of its edges was poor, thus rendering it impossible to set the cross hairs on it with accuracy. The best combination of intensity and definition was obtained by avoiding prominences and working only on very clear days.

The observations were made by the ordinary microscopic method, the D_3 line being compared with the best solar standard lines in the field of view. The wave lengths of these standard lines, as taken from Professor Rowland's "Table of Standard Wave Lengths" (*Astr. and Astro.-Phys.*, vol. xii., p. 321, and *Phil. Mag.*, V., vol. xxxvi., p. 49) were—

Fe	5916.475	Fe	5862.580
Fe	5914.384	Fe	5859.810
Fe	5905.895	Ba	5853.903
Na.D ₁ ..	5896.154	Average value	5887.028

Seventeen series of measurements were made, in each of which equal numbers of observations were taken on diametrically opposite points of the sun's limb in order to eliminate the effect of rotation.

The wave length of D_3 was calculated from each of these series by Professor Rowland's method of interpolation, on the assumption that, for the space used, the spectrum was essentially normal. The average of the seventeen values thus found gives

$$5875.939 \pm 0.006$$

for the wave length of the D_3 line, the probable error being calculated from the deviations of the several values from the mean in the usual manner.

To test the accuracy of the observations and method of calculation, the wave length of the mean line was computed from the observations and found to be 5887.027, a value which differs only by 0.001 from the average of the wave lengths of the standard lines used, 5887.028.

I am indebted to Professor H. A. Rowland and Dr. J. S. Ames for permission to use apparatus and for suggestions, and to Mr. W. S. Day for aid in making the observations.

* From the *American Journal of Science*, vol. 1., November, 1895.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 7.)

The Method of Ascertaining whether Chlorine be present or no in the Oxygen Liberated during the Dissociation of Chlorate and Perchlorate of Potassium by the Action of Heat.

THE research on the presence or absence of chlorine in the oxygen liberated during the dissociation of chlorate and perchlorate of potassium is one of a most delicate nature. As a matter of fact, the oxygen given off is always cloudy, and it generally contains chlorate, perchlorate, and chloride of potassium. In addition to this, the strong smell of ozone may lead one astray. I have only succeeded in my efforts by working in a well polished platinum retort. When one decomposes chlorate or perchlorate in a glass retort, even when annealed, there is always chlorine present. In order to completely free the oxygen from the potassic compounds which make it hazy, I used asbestos packing, such as I used when analysing the oxygen produced from chlorate, when decomposing this salt by the action of heat.*

The apparatus I used was arranged as follows:—I fitted the long neck of the platinum retort, filled with the potassic salt to be separated, and which had been previously washed, as far as possible into a large glass tube, 50 c.m. long. On the other end of this tube another tube, 5 m.m. inside diameter and bent to a slight obtuse angle, was fused; at this end there was a cylinder, almost the same diameter as the large tube, filled with pumice-stone which had been calcined after being soaked in concentrated sulphuric acid. Above this cylinder of pumice-stone was a pile of strongly heated asbestos felt, 25 c.m. high, and so packed as to allow the oxygen to filter freely, whilst stopping the saline dust.

The bent tube, fused to the large tube into which the neck of the platinum retort was fitted, was connected with one of the two holes in a glass plug, 8 c.m. in diameter, ground into a glass flask, containing a platinum dish one third full of water saturated with absolutely pure ammonia. This tube reached nearly to the surface of the ammoniacal liquid.

To the other hole in the plug was fitted a tube bent at an acute angle, communicating, by means of a rubber tube, with a Liebig apparatus containing a moderate quantity of pure water. The free end of the Liebig tube was in communication with a water-pump, which could be worked as slowly or as quickly as one wished.

Since the neck of the platinum retort, though reaching very far into the large tube, 50 c.m. long, did not completely fill the opening, the inner atmosphere could escape, and the outer atmosphere could penetrate inside, according as the inside pressure was greater or less than the outside pressure.

Profiting by experience, I regulated the aspiration so as to have constantly an excess of pressure inside the apparatus. To attain this result, I was guided by the smell of ozone, which is produced at the place where the neck of the platinum retort enters the tube; one could even detect an evolution of saline fumes at this part, when the dissociation of the potassic salt took place too rapidly for the amount of gas drawn through the apparatus.

I found I was obliged to adopt the above-described apparatus, and especially to use a platinum vessel to hold the concentrated solution of pure ammonia, because it is impossible to leave this solution in an ordinary glass vessel without the glass being attacked and sensibly dissolved.

For instance, if one evaporates in a platinum dish a concentrated solution of ammonia, which has been left for several hours in a glass beaker, one gets a white, strongly alkaline residue, made of silicate of calcium and sodium; and when the dissolved ammonia contains a very small quantity of chloride of ammonium, it is so far decomposed that the white residue does not contain any traces of it, and its chlorine is in the form of chloride of calcium and sodium.

When dissociating chlorate and perchlorate of potassium in the apparatus I have just described, by means of a well-regulated temperature, one sees these varying facts, according as the salts are absolutely pure, or contain iron, manganese, copper, silica, or silicates.

Do these salts bring the impurities mentioned above? as is the case with chlorate made by simple successive crystallisations in pure water, whilst the temperature of the melted chlorate is so high that the platinum retort emits the singing noise always heard during the dissociation of salt and the liberation of oxygen, when the gas, penetrating into the ammoniated atmosphere, makes from the beginning to the end of the decomposition white fumes, of which a part only dissolves in the ammonia in the platinum vessel; the remainder is carried off by the current of gas through the Liebig apparatus, so as only to be partly dissolved in the water it brings.

When evaporating ammonia, over which oxygen has passed, on a water bath in the covered platinum dish, there remains a white residue, quite volatile at a low temperature, and displaying all the properties of chloride of ammonium.

The water used to wash the gas, having been saturated with nitric acid, was clouded by the addition of a few drops of a 10 per cent solution of nitrate of silver.

Thus, as I demonstrated in my "Researches on the Reciprocal Ratios of Atomic Weights," there is no doubt as to the presence of chlorine in the oxygen liberated during the dissociation of chlorate of potassium containing impurities in the salt, made by successive crystallisations in pure water. As the liberation of chlorine shows itself until the end of the operation, it necessarily follows that the decomposition of perchlorate made during the dissociation of chlorate must also take place with the liberation of chlorine. I have elsewhere stated that siliceous perchlorate of potassium, when decomposed by heat, yields oxygen mixed with traces of chlorine. The facts are quite different when substituting pure chlorate and perchlorate for even slightly siliceous chlorate.

When pure chlorate is decomposed by the action of heat, either slowly or more or less quickly, the oxygen drawn through the asbestos felt, on coming in contact with ammonia, suddenly forms a very slight haze, probably due to the action of the ozone in the oxygen on ammonia, which, according to Carius, makes nitrite of ammonium, but never a smoke such as is seen when chlorine mixed with oxygen comes in contact with ammonia gas.

So long as the aspiration is not great, the oxygen reaches the Liebig apparatus quite transparent, and passes through it without producing the slightest haze.

I evaporated on a water bath, in a covered platinum dish, the ammonia across which had passed oxygen from the dissociation of:—1st, 60 grms.; 2nd, 100 grms.; 3rd, 150 grms. of pure chlorate of potassium; 4th, 57 grms. of pure perchlorate of potassium. I effected the decomposition of the pure perchlorate under the same conditions as the chlorate, at the request of M. Berthelot. During all four trials the evaporation was completed without leaving any residue. The surface of the platinum dish was washed with pure water; this was found to be neutral to litmus paper, and remained quite clear after the addition of five drops of a 10 per cent solution of nitrate of silver, and remained clear and colourless after being exposed to direct sunlight—a phenomenon only seen so long as the liquid contains no trace of chloride of silver.

The water in the Liebig apparatus, through which the oxygen had passed, having been neutralised by nitric acid,

* "Recherches sur les Rapports Réciproques des Poids Atomiques" (Bulletins de l'Académie Royale de Belgique, 2e Sér., t. x., p. 109).

and having then had some nitrate of silver added, kept quite clear in all four experiments; it remained clear and colourless after a long exposure to direct sunlight.

It is therefore proved that *pure* chlorate and perchlorate of potassium can be dissociated in a *pure* and *polished* platinum dish without liberating a trace of chlorine. I have further found that the chloride of potassium made at the same time is *absolutely neutral* to colour tests. These two facts, which I was unable to discover for more than a third of a century, prove the constancy of the ratio between the weights of chlorine and potassium in chlorate, perchlorate, and chloride of potassium, and fully confirm the conclusions I drew from the action of sulphurous acid on chlorate, bromate, and iodate of silver, made under normal conditions. It was with the hope of being able to show the accuracy of the law of definite proportions, without having resource to chemical action and weighings, that decided me to devote much time and great care to finding out, whether or no, chlorate and perchlorate could, *by the action of heat alone*, be changed into chloride, without liberating an appreciable trace of chlorine.

Spectroscopic Study of Potassium.—Character given to Flames by Compounds of Potassium.

The Luminous Spectrum of Potassium.—Chemists state that potassium compounds give a purplish-blue colour to the envelope of the flame of a well-made Bunsen burner. I must say I was surprised to find that *chlorate* and *perchlorate* of potassium, from which I had eliminated all solid compounds and sodium, when put into the outer part of this flame on a loop or spiral of fine platinum wire, gave it a *pale* or *sky* blue colour, and *chloride* of potassium a *deep* blue colour. These colours were also seen in a pure hydrogen flame, and in a hydrogen and air, oxyhydrogen, and oxy-coal gas blowpipe flames.

Experiments most carefully conducted, using the purest potassic compounds, have convinced me that the blue tint is stronger as the mass of potassium is *greater* at a similar temperature, and it becomes *fainter* as the temperature is raised, when the mass is the same. Beyond the fusing point of platinum the colour of an oxyhydrogen blowpipe flame charged with potassium is very pale blue; it is even paler than incandescent hydrogen; thus one is tempted to ask whether the vapour of potassium compounds is still coloured when raised to the very highest temperature, such as the fusing point of iridium.

Spectrum analysis of potassium *flames*, coloured light or dark blue, shows the spectrum of potassium compounds, as it was described and measured by M. Lecoq de Boisbaudran in 1874, and in 1875 by M. Bunsen, in his memoir "Spektal-Analytische Untersuchungen," that is to say, it consists of a *red* line, a *pale red* band, and a very faint *purple* line. *The sodium D line is not present.*

Notwithstanding that I had seen the pale red band, mentioned by M. Bunsen and Lecoq de Boisbaudran as being due to potassium, I always had doubts as to the origin of this band. In fact, when making a spectrum analysis of a potassic hydrogen flame, at a temperature where the gas no longer shows a *continuous spectrum*, and shutting out rays from the support, and using a sufficiently narrow slit, the spectrum consists of an *absolutely dark band* in which only the *red* line at 21·5 divisions on the micrometer scale of my spectroscope, corresponding to 17·4 on that of M. Bunsen, and the *purple* line at 140·50 on my scale, corresponding to 153·5 on that of M. Bunsen, are visible.

However narrow the slit might be, whenever we make a spectrum analysis of an incandescent hydrogen flame in which a potassium compound has been volatilised, the spectrum is *continuous*, showing the red line at 21·5 on my spectroscope, corresponding to 17·4 on that of M. Bunsen, and the purple line at 141·5 on my spectroscope, corresponding to 153·5 on that of M. Bunsen. *In both cases I have noticed the absence of the red band and the sodium line.*

I was able to show that the flames of pure chlorate and

perchlorate of potassium were *pale blue*, and that the faint red band and the sodium D line were absent from the potassium spectrum during the months of November and December, 1878, December, 1880, and November and December, 1882 and 1883. M. Rommelaere, who assisted me in this work noticed the same facts.

To obtain the double condition, *i.e.*, the flame coloured light blue, and the sodium line not present, there are required—(1st) the air very pure; (2nd) nascent potassium compounds.

The method which gave me the best results consisted in plunging a fine platinum wire loop, covered with iridium, previously heated to whiteness to drive off sodium brought by the air, into a saturated and boiling solution of the potassic compound, made when sheltered from atmospheric dust, and in putting this loop at once into the outer part of an oxyhydrogen flame or blowpipe, with an excess of hydrogen.

If the salts adhering to the platinum loop, or the bulk of it, are kept under a bell-jar in contact with air, after a few hours, and sometimes after half an hour, they show, on spectrum analysis, unmistakable signs of the presence of sodium absorbed from the air, and they colour flames a *purplish blue*. Chlorate, perchlorate, and chloride of potassium, which were quite free from sodium at the time of their preparation, when put into bottles with ground-glass stoppers, and opened from time to time, and kept for six months in a closed cupboard, showed the sodium line, on spectrum analysis, as strongly as chlorate, perchlorate, nitrate, and monopotassic tartrate, which had been purified by ten successive crystallisations under cover from atmospheric dust, and they coloured the hydrogen flame a purplish blue. *The contamination of potassium compounds by atmospheric sodium is enough to cause them to sensibly colour a flame yellow if the action has lasted long enough.*

Potassium salts then resemble platinum, silver, carbon, &c., which also absorb sodium from the air. The experiments I describe further on show that it is just the same with all the bodies on which I have carried on my investigations.

When one tries to reproduce the phenomena I have just described, in air contaminated by mineral and organic dust in suspension, as is nearly always the case in places where work is carried on, the introduction of the purest potassium compounds gives a varying colour to the flames, which are frequently greenish yellow at first, changing to strong violet after a few moments, and keeping this colour until the potassic salt has completely disappeared. In this case the sodium line, and *often* an *incomplete* calcium spectrum, is *always* seen accompanying the characteristic potassium lines. The calcium spectrum is more marked, when some hydrogen which has been impregnated with hydrochloric acid by passing through a saturated solution of the same, is introduced into the potassic flame.

The colour given by potassium compounds to coal-gas or pure hydrogen, burning in an excess of air, is then pale blue, deep blue, or violet blue, according to the state of the air and the potassic compounds.

I mentioned above that the very purest of these compounds, when kept for some time in closed glass vessels, with emery-ground stoppers, but opened from time to time, give unmistakable signs of the presence of sodium. I ought to add that, in this case, they give to the flame that violet colour looked upon by all chemists as a distinctive characteristic of potassium compounds. I have tried to find the reason for this difference in colour. Having frequently noticed the formation of an incomplete calcium spectrum during the production of the violet flame, I thought at one time that this colour was due to the presence of traces of calcium in the potassium compound, and in truth the complete elimination of calcium is very difficult. But I soon found I was not able to detect the calcium spectrum, or any of the characteristic lines of this metal, in the spectrum of violet flames con-

taining a given potassium compound. One day I volatilised *five grms.* of chloride of potassium made from pure perchlorate in an oxyhydrogen blowpipe; after some seconds, the flame, which was first deep blue, then light blue, became intensely violet. During the few minutes occupied in volatilisation, I watched the spectrum, and although I was obliged to raise the temperature in the first place so high that I melted the concave sheet of platinum in places, and in the second place I used a *cup of pure iridium containing a hollow cone of this metal, heated almost to its fusing point*, I was unable for a single instant to see the calcium spectrum or even any one of its characteristic lines in the very bright potassium spectrum.

A part of the same chloride of potassium made from perchlorate, when volatilised several months afterwards, coloured the flame blue throughout the experiment, and the colour became fainter as the temperature was raised; this colour never passed the azure tint shown at the same time by an oxyhydrogen blowpipe flame free from all traces of potassic vapour. Thanks to the exceptional purity of the air on this occasion, I was able to repeat the experiment twice, with the same result.

Unless the potassium rays masked the weak calcium rays, which is not impossible when considering the analogous facts noted, I can only attribute the difference in colour, given to the *same* flame by the *same* chloride, to sodium brought by air currents.

I give the facts as they appear from my own observations, thoroughly checked by myself and by other persons who have witnessed them.

Whatever may be the cause of the variation in the colouring of flames by pure potassic compounds, the fact, the investigation of which has been the object of my chemical and spectroscopic researches on potassium, can be no longer doubted. I have found beyond a doubt that it is possible to get potassium compounds which, when put into *flames*, give no trace of the double D sodium line, and that at the very highest temperatures of hydrogen or coal-gas burning in pure oxygen. The double D line is only seen in the potassium spectrum, when the air, or the compound being examined, contains sodium as an impurity, as is the case with nitrate of potassium, which I could not obtain without a slight trace of sodium, and which coloured a hydrogen flame pale blue tinged with violet.

My researches enable me to state these facts in a positive formal manner.

The spectra of chlorate, perchlorate, chloride from perchlorate, chloride from chlorate, and chloride from chloroplatinate of potassium are identical; they consist of either a dark or bright continuous spectrum, both marked by two lines, according as the spectrum analysis is made of a potassium flame in which the hydrogen either is *not* or *is* made incandescent. In the latter case the illumination of the spectrum is *partial* or *total*, according as the compound is put and the analysis made outside or inside the inner cone of an oxyhydrogen or oxy-coal-gas blowpipe.

Potassium then behaves as a body distinct from sodium; it is not reducible to sodium by heat. Much evidently depends on the conditions under which researches can actually be carried on.

(To be continued).

Action of Chlorocarbonic Oxide upon some Derivatives of Sulphonic and Sulphinic Acids.—P. Tischendorf.—The author has attempted to extend the formation of urea from chlorocarbonic oxide and ammonia to some ammoniacal derivatives of aromatic sulphoacids. He has to this end examined the behaviour of phenylsulphonamide (melting-point 148°), *p*-tolylsulphonamide (melting-point 107°), phenylsulphonphenylamide (melting-point 134°), and para-tolylsulphonphenylamide (melting-point 99°), but in only two cases has he obtained the results expected.—*Journ. f. Prakt. Chem.*

THE PREPARATION OF PERCHLORIC ACID AND ITS APPLICATION TO THE DETERMINATION OF POTASSIUM.*

By D. ALBERT KREIDER.

(Concluded from p. 9).

IN applying perchloric acid, thus prepared, to the determination of potassium according to the treatment suggested by Caspari (*loc. cit.*), very satisfactory results were obtained. Briefly, the method is as follows:—The substance, free from sulphuric acid, is evaporated to the expulsion of free hydrochloric acid, the residue stirred with 20 c.m.³ of hot water and then treated with perchloric acid in quantity not less than one and one-half times that required by the bases present, when it is evaporated with frequent stirring to a thick syrup-like consistency, again dissolved in hot water, and evaporated with continued stirring till all hydrochloric acid has been expelled and the fumes of perchloric acid appear. Further loss of perchloric acid is to be compensated for by addition of more. The cold mass is then well stirred with about 20 c.m.³ of wash alcohol—97 per cent alcohol containing 0.2 per cent by weight of pure perchloric acid—with precautions against reducing the potassium perchlorate crystals to too fine a powder. After settling, the alcohol is decanted on the asbestos filter and the residue similarly treated with about the same amount of wash alcohol, settling and again decanting. The residual salt is then deprived of alcohol by gently heating, dissolved in 10 c.m.³ of hot water and a little perchloric acid, when it is evaporated once more with stirring until fumes of perchloric acid rise. It is then washed with 1 c.m.³ of wash alcohol, transferred to the asbestos, preferably by a policeman to avoid excessive use of alcohol, and covered finally with pure alcohol: the whole wash process requiring about 50 to 70 c.m.³ of alcohol. It is then dried at about 130° C. and weighed.

The substitution of a Gooch crucible for the truncated pipette employed by Caspari will be found advantageous; and asbestos capable of forming a close, compact felt should be selected, inasmuch as the perchlorate is in part unavoidably reduced, during the necessary stirring, to so fine a condition that it tends to run through the filter when under pressure. A special felt of an excellent quality of asbestos was prepared for the determinations given below, and seemed to hold the finer particles of the perchlorate very satisfactorily.

A number of determinations made of potassium unmixed with other bases or non-volatile acids are recorded in the following table:—

KCl taken. Grms.	Volume of filtrate. C.m. ³ .	KClO ₄ found. Grms.	Error on KClO ₄ . Grms.	Error on KCl. Grms.	Error on K ₂ O. Grms.
0.1000	54	0.1851	0.0008—	0.0004—	0.0003—
0.1000	58	0.1854	0.0005—	0.0002—	0.0002—
0.1000	51	0.1859	0.0000	0.0000	0.0000
0.1000	50	0.1854	0.0005—	0.0002—	0.0002—
0.1000	48	0.1859	0.0000	0.0000	0.0000
0.1000	52	0.1854	0.0005—	0.0002—	0.0002—

Considerable difficulty, however, was experienced in obtaining equally satisfactory determinations of potassium associated with sulphuric and phosphoric acids. As Caspari has pointed out, the sulphuric acid must be removed by precipitation as barium sulphate before the treatment with perchloric acid is attempted, and unless the precipitation is made in a strongly acid solution, some potassium is carried down with the barium. Phosphoric acid need not be previously removed; but to secure a nearly complete separation of this acid from the potassium, a considerable excess of perchloric acid should be

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. xlix., June, 1895.

left upon the potassium perchlorate before it is treated with the alcohol. When these conditions are carefully complied with fairly good results may justly be expected. Below are given a number of the results obtained.

Compounds taken. Grms.	Vol. of filtrate. C.m.s.	KClO ₄ found. Grms.	Error on KClO ₄ . Grms.	Error on KCl. Gims.	Error on K ₂ O. Grms.
KCl=0.10					
CaCO ₃ =0.13	50	0.1887	0.0028+	0.0014+	0.0009+*
MgSO ₄ =0.13	82	0.1875	0.0016+	0.0008+	0.0005+*
Fe ₂ Cl ₆ =0.05	80	0.1861	0.0002+	0.0001+	0.0001+†
Al ₂ (SO ₄) ₃ =0.05	80	0.1843	0.0016-	0.0008-	0.0005-†
MnO ₂ =0.05	92	0.1839	0.0020-	0.0010-	0.0006-†
HNa ₂ PO ₄ .					
12H ₂ O=0.40	60	0.1854	0.0005-	0.0002-	0.0002-†

In the last three experiments of the above table the amount of perchloric acid was about three times that required to unite with the bases present, and the phosphoric acid subsequently found with the potassium was hardly enough to appreciably affect the weight, although its absolute removal was found impossible.

The kindly direction and frequent advice of Professor F. A. Gooch during the investigation is gratefully acknowledged.

A VOLUMETRIC METHOD FOR LEAD ANALYSIS.

By ALFRED C. BEEBE,
Chemist to the Chicago and Aurora Smelting and Refining Company.

As I have found the existing volumetric methods for the analysis of lead more or less unsatisfactory, on account of the lack of a sharp characteristic end reaction, I have devised the following scheme, which combines accuracy with rapidity.

It depends upon titrating a solution of acetate of lead free from alkali salts by means of ferrocyanide of potassium, using a saturated solution of uranium acetate as an indicator. The end reaction, which is formed by adding a drop of the solution, being titrated to the uranium solution on a porcelain plate, is a delicate pink, changing, after standing some time, to brown. The ferrocyanide solution can be standardised with either lead sulphate or lead acetate. Eleven grms. of ferrocyanide in one litre of water will give about a 1 per cent solution. The uranium acetate solution should have a little free acetic acid in it, or the sharpness of the end reaction is affected.

The method for analysis is as follows:—Dissolve the substance to be analysed in nitric acid, using a little hydrochloric acid if necessary. When the decomposition is complete add sulphuric acid and evaporate till white fumes of sulphuric anhydride are given off. Dilute with water and cool. Add to the liquid its own volume of common alcohol and allow it to stand a short time. Filter and wash with hot water. Then wash the residue into about 50 c.c. of a cold saturated solution of ammonium carbonate with some of the carbonate solution. Stir frequently and vigorously for about 15 minutes. Filter, and wash both residue and filter very thoroughly with hot water. Dissolve the lead carbonate in hot dilute acetic acid. Cool and titrate with a solution of ferrocyanide of potassium.

Barium and calcium do not interfere with the results. Arsenic is eliminated by the method of treatment. Antimony compounds can be made soluble by the use of tartaric acid in the decomposition of the substance. Should iron, copper, or zinc be present, a very thorough washing of the lead sulphate will be necessary. If any substance is found to interfere seriously with the results, the copper and arsenic groups can be separated from their acid solu-

tion by means of sulphuretted hydrogen. The resulting sulphides can be dissolved in nitric acid and the regular method of analysis followed.

I have used the method as given above with excellent results. As, however, there are many artificial and natural products I have had no opportunity to try, I will regard it as a favour if other chemists will send me criticisms or suggestions concerning this scheme.—*Engineering and Mining Journal*.

ON THE PROLONGED ACTION OF LOW HEATING ON DETONATING GAS.

By VICTOR MEYER and WILHELM RAUM.

It is well known that in heat detonating gas is converted into water, whilst in the cold it remains unchanged. But whilst there is no doubt as to its condition in heat there prevail two opinions concerning its behaviour at common temperatures. The great body of chemists hold that it undergoes no reaction, whilst the majority of physical chemists are convinced that a formation of water occurs, but that the speed of the reaction is so small that it remains unperceived. For this assumption evidences are not wanting. For instance, the reaction becomes at once perceptible by katalysis, by the addition of platinum black, and attains a considerable rapidity. But it is probable that substances which act katalytically never introduce a reaction which previously does not exist, but merely increase its rapidity. That the reaction is not perceptible in the cold need not surprise us, since all experience in this region teaches us that the rapidity of chemical reactions decreases remarkably with a reduction of temperature. Theoretical considerations teach us the same. Hence it is probable that the reaction on descending from 500°—at which temperature it takes place with moderate rapidity—to the temperature of a dwelling-room, undergoes an enormous retardation, so that recognisable quantities of water would appear only in the course of centuries or of thousands of years.

Nernst has recently pointed out that it is not indifferent whether we consider a reaction as absolutely non-existent or as taking place with an immeasurably small rapidity.

An exact demonstration might be given by keeping detonating gas for a very long time and observing the appearance of a contraction. I have already shown that this phenomenon does not occur within the lapse of two years, and according to Berthelot the same result has been obtained in an observation continued for many years.

As time is wanting to extend the experiment for the necessary duration, we had to be contented with an approximate experiment based on the following consideration. We first ascertained the temperature at which, in common language, detonating gas no longer reacts, *i.e.*, undergoes no change on observation for several days. This temperature we found at 300°; on heating specimens of detonating gas uninterruptedly to this temperature for 10 days, we could not observe any formation of water. Next, detonating gas was exposed to this temperature for a much longer time without interruption (65 days and nights). Setting out with the opinion that at temperatures which lead apparently to no reaction, still such a reaction would be manifested on extremely long heating, we expected that here a formation of water would appear. *This was in fact the case.* If, therefore, at 300°—which temperature shows no formation of water in observations of an ordinary duration—a reaction becomes manifest on a very protracted heating, the assumption seemed admissible at still lower temperatures, and that formation of water would be detected on a further prolongation of the experiment.

The performance of these experiments presented various technical difficulties, and did not prove so simple as we

* The residue showed phosphoric acid plainly when tested,

† Only traces of phosphoric acid found in the residue.

at first expected. The investigation was always effected according to the method described by Victor Meyer, Krause, and Askenasy (*Ann. der Chemie*, cclxiv., 85, and cclxix., 49). The specimens of detonating gas were heated in vessels sealed hermetically, and having capillary appendages of one-third m.m. internal diameter. The gas was prepared and electrolytically purified from ozone and dried over sulphuric acid. The usual precaution was observed of employing check bulbs, sealed under identical conditions, and preserved unchanged, in order, on opening the bulbs, to be independent of the state of the thermometer or barometer, was here employed. In the former investigations it was shown that the formation of water commenced very plentifully at 518° (vapour of P_2S_5), slowly in vapour of sulphur (448°), and scarcely perceptibly in mercurial vapour (350°). Our experiments showed that at the last temperature the quantities of water formed were not inconsiderable. We obtained in 50 hours 1.6 per cent; in 60 hours 1 to 1.6 per cent; in 120 hours 1.9, 16.4, 0.5, 0.7, 1.2 per cent.

The heating to 300° —particularly important for our purpose—was first undertaken in the vapour of diphenylamin (boiling point 305°). On heating a number of specimens for ten days we obtained no recognisable quantities of water. For a much more prolonged experiment diphenylamin seemed less convenient, as after some time it becomes resinified, and even in the above mentioned relatively brief experiment it had to be several times renewed. For prolonged experiments a metal bath was therefore used with a suitable regulator. During 65 days the temperature never rose more than 4° or 5° above 300° .

Of the six bulbs employed only three survived the experiment, whilst the remainder burst. The quantities of water produced in the former were respectively 9.5, 0.4, and 1.3 per cent.

We must further mention that we made an experiment by heating bulbs filled with detonating gas for 218 days and nights, without intermission, in a boiling water-bath. There was no perceptible formation.—*Berichte*, xvii., p. 2804.

TELLURIUM: ITS SEPARATION FROM COPPER RESIDUES, WITH NOTES ON SOME NEW REACTIONS.

By CABELL WHITEHEAD.

TELLURIUM, which a few years ago was classed as a rare metal, is now known to be distributed over a very wide area, not only in our western states, but also in the gold-producing states of the east. It occurs in the free state, and also combined with gold, silver, bismuth, and many other metals. In the state of Colorado, tellurium is found in combination with gold and silver to such an extent that the ores in many districts are rendered unfit for amalgamation, and smelting and chlorination has to be resorted to. The separation of silver and gold from low grade telluride ores is a problem which, up to the present time, has baffled the skill of the metallurgists of the world. A few of the difficulties may be mentioned as follows:—Tellurides do not give up their gold to mercury, cyanide, or chlorine; they concentrate badly, a large percentage of the value being lost as slimes. They are difficult to roast, on account of their low melting-point, and the loss of gold during the removal of the tellurium. The usual course is to smelt this class of ore either with lead or copper ores. It is to the latter method I will call especial attention in this paper.

In order to work the copper ores of the west economically, they are smelted with gold- and silver-bearing ores, which act as flux, and also enrich the matte produced to a point where the cost of refining the copper is more than covered by the value of the precious metals contained. In this way large amounts of tellurium enter the

matte. These mattes are Bessemerised in the west, and copper brought east to be refined by electrolysis. It contains from 98.5 to 99.5 per cent copper, about 100 ounces of silver, and 3-10ths ounce of gold per ton. The impurities are arsenic, antimony, lead, bismuth, tellurium, and selenium. The average amount of tellurium is not far from 0.04 per cent, or 0.8 of a pound per ton. With the possible exception of the native copper of Lake Superior, it is doubtful if any copper produced is free from tellurium; this is certainly true of that from sulphide ores. I have already described a method for estimating the tellurium under these circumstances (*Journ. Amer. Chem. Soc.*, xvii., 280, 1895).

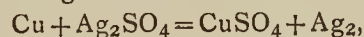
The electric refining of such copper is carried on at Anaconda, and at the Boston and Montana Copper Co. works at Great Falls, Montana; the Baltimore Electric Refining Co., Baltimore, Maryland; the Bridgeport Copper Co., Bridgeport, Conn.; and the Ansonia Refining Co., Ansonia, Connecticut; the Central Falls Electric Refining Co., Central Falls, Rhode Island; the Washburn and Moen Co., Worcester, Mass.; and perhaps others.

In the Hayden process a bath of dilute copper sulphate, acidified with sulphuric acid, is employed, in which is inserted an anode of rolled black copper and a cathode from a strip of pure copper, each being connected with the electric generator, while disconnected plates of black copper are suspended in the bath between the two electrodes. When the current is on, solution takes place, not only at the anode but on all the disconnected plates interposed between the electrodes, and, what is more interesting, this solution takes place on those surfaces of these plates which face the negative electrode, while the deposition of the pure copper takes place on the surface of the adjacent plate which faces the positive electrode. When the copper goes into the solution in its bath, small amounts of some of the impurities in the copper enter into solution with it, but the greater portion remains either in the metallic state or are converted into oxides or basic salts which fall to the bottom of the bath, where they form a black slimy residue.

The commercial refining of these residues is carried out as follows:—

After screening out the coarser copper, the slimes are boiled with a 20 per cent solution of sulphuric acid in a lead-lined tank by live steam, air being drawn in with the steam by means of a peculiar injector. During this boiling, practically all of the antimony, arsenic, and bismuth salts, together with copper in the oxidised condition, and that small portion of metallic copper which has been oxidised by the injected air, go into solution.

After about one hour's boiling, a solution of silver sulphate is run in and steam applied for some minutes, whereby, according to the reaction—



the metallic copper still remaining is rapidly and completely converted into copper sulphate. Any excess of silver sulphate is removed by the addition of a fresh portion of slimes, when the solution is drawn off and the residue washed until free from copper salts. This residue, which has now lost the slimy adhesive properties which characterised it, and which consists of gold, silver, tellurium, and lead sulphate, is pressed on a filter-press. The pressed cakes are dried in an oven and then melted in a furnace, having a bed made of Portland cement, which is so arranged that a blast may be turned on. This quickly removes all but a trace of the lead present, together with portions of the tellurium and selenium.

The resulting bullion is poured into shoe-bars, weighing about 300 ounces each; it is about 950 fine in silver, and 10 parts of gold. When cool these bars are dissolved in hot sulphuric acid, in a cast-iron kettle; and when solution is complete the liquid is allowed to cool and settle for several hours, during which the gold falls to the bottom and the tellurium crystallises out in white lustrous

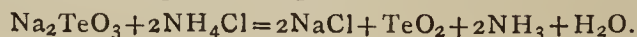
crystals of tellurous oxide. The first portion of the clear liquid is drawn off and precipitated by metallic copper, and the silver melted into bars 990 fine. The remainder is used in treating a fresh portion of the slimes.

The gold and the tellurous oxide are allowed to accumulate in the kettle until several hundred ounces are at hand, when they are removed and washed with dilute sulphuric acid and water, to remove silver, copper sulphate, and tellurous oxide, and afterwards boiled in a small kettle with concentrated sulphuric acid, to remove the remaining portion of silver and tellurium. When cool, and the gold has settled, the acid is again drawn off and the residue washed until free from tellurium and silver sulphates. The gold is now melted with borax and nitre, by which any remaining traces of lead and tellurium are oxidised and slagged off, leaving fine gold, over 990 fine, the impurity being silver.

The washings from the gold residue contain the tellurium as tellurous oxide or tellurous sulphate. The tellurium may be obtained from these in two ways, after the removal of the silver as chloride. First, by precipitation with copper; second, by passing sulphur dioxide through the solution. It is better to use the first method, as large quantities of sulphur dioxide are very disagreeable to handle, and as the tellurium thus precipitated in the presence of copper is not pure and requires a further treatment. The metal used in this work was produced by inserting bars of copper into the solution and boiling with steam, a precipitate of cuprous telluride being obtained as a black powder. This was dried and then boiled with a 5 per cent solution of sulphuric acid, to remove the copper which had been oxidised during the drying process. After filtering, the mass is again moistened with 5 per cent sulphuric acid, and subjected to atmospheric oxidation with frequent stirring, then boiled again with more sulphuric acid, and washed; this process is repeated until the copper is eventually very completely removed. Any copper left will combine with tellurium when fused, and cause loss. The residue is now dried, mixed with three times its weight of sodium carbonate and one-fourth its weight of charcoal, melted in a French clay crucible to quiet fusion, brought almost to a white heat, and the melt poured into a suitable mould. The cooled mass is crushed to a powder and the sodium telluride formed, dissolved out with boiled water; a great amount of heat is developed during the solution. The solution thus produced, which possesses a rich port-wine colour, is filtered off, and the tellurium precipitated in the metallic state, by the passage of a current of air, as a fine grey powder, looking not unlike finely-powdered galena. The tellurium is filtered and boiled with dilute hydrochloric acid, to remove traces of iron, alumina, &c., washed and boiled for several hours, with a concentrated solution of potassium cyanide, which removes selenium and most of the gold present. After drying, the tellurium is melted, without flux, in a French clay pot; the fine particles are made to run together by stirring; only a low temperature is necessary, and the loss by volatilisation is small. The metal still contains traces of impurities, the chief of which is gold. This would indicate that sodium telluride is a solvent of metallic gold, but this has not yet been proven. The tellurium is further purified by distillation in hydrogen gas.

New Reactions of the Salts of Tellurium.

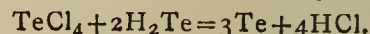
If to a solution of the sodium or potassium tellurite is added a solution of an ammonium salt, such as the chloride or nitrate, a white precipitate is thrown down, which on boiling becomes granular.



A small amount of tellurium dioxide, or a metal which can be precipitated by sulphur dioxide, remains in solution. It is the intention of the writer, as soon as possible, to examine and compare the properties of the metal

from this fractional precipitation. While it is probable that tellurium oxide is slightly soluble in the alkali salts formed, which would explain incomplete precipitation, in view of the growing belief in the compound nature of tellurium, this reaction is deemed worthy of further investigation.

In an effort to purify tellurium, based upon the well-known property of hydrogen telluride of precipitating many of the metals from solution, the following reaction was observed, in addition to the one expected.—



By passing this gas for some time into a solution of tellurium chloride, made slightly acid with hydrochloric acid, there was obtained a precipitate of tellurium and tellurides and a solution, from which sulphur dioxide threw down a precipitate of tellurium. After distillation in hydrogen, I propose to determine the atomic weight of this purified metal.

When potassium ferrocyanide is added to tellurium chloride no change is observed at first, but after a few hours Prussian blue is formed in large quantities.

Aluminum Telluride.

Tellurium when heated with aluminum combines with explosive violence, forming a chocolate-coloured, difficultly fusible compound, having the following composition by analysis:—

	Per cent.
Aluminum	12.78
Tellurium	87.22
	<hr/>
	100.00

This corresponds closely to the formula Al_2Te_3 , which requires—

	Per cent.
Aluminum	12.58
Tellurium	87.42
	<hr/>
	100.00

The violent chemical action attending its formation, joined with the fact that its composition remains constant, even in the presence of a large excess of aluminum, would indicate a true chemical combination and not an alloy, in the accepted sense. It is hard and brittle, can be easily ground to powder. When exposed to moist air it is slowly decomposed with the liberation of hydrogen telluride. When thrown into water, hydrogen telluride is rapidly given off according to the following reaction:— $\text{Al}_2\text{Te}_3 + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{Te}$, which corresponds to the well-known sulphur reaction $\text{Al}_2\text{S}_3 + 3\text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{S}$. While comparing these two reactions, it may be noted that hydrogen telluride is much more easily decomposed by oxygen than hydrogen sulphide. For example, in treating aluminum telluride with water which has not been boiled, fully one-half of the tellurium remains as metal:— $\text{H}_2\text{Te} + \text{O} = \text{H}_2\text{O} + \text{Te}$. When treated with 95 per cent alcohol no reaction takes place, even on boiling. This would seem to be the best one of the tellurides from which to make the organic salts, as it does not decompose in the air so quickly as the alkali tellurides.

Separation from Copper by the Electric Current.

Tellurium is easily deposited by the current either from acid or alkaline solutions; even the feeblest current throws out the metal, but unfortunately not in the reguline state.

It has been found possible to separate tellurium from copper by adding an excess of sodium hydroxide and about 3 grms. of potassium cyanide for each grm. of copper present. With this solution, a current such as is used for depositing copper will throw out all the tellurium present, as a black non-adherent precipitate. After twelve hours the tellurium is filtered off and weighed, either as metallic tellurium on a weighed filter or as tellurium dioxide. The solution is now made slightly acid

with sulphuric and the copper precipitated in the usual way. If the proper amount of potassium cyanide has been added, and the current has not been allowed to run too long, the tellurium is perfectly free from copper, and if the current is strong enough none of it will adhere to the cathode.—*Journ. Amer. Chem. Soc.*, vol. xvii., p. 849.

NOTICES OF BOOKS.

Gas Manufacture: The Chemistry of. A Practical Handbook on the Production, Purification, and Testing of Illuminating Gas, and the Assay of the By-products of Gas Manufacture. For the Use of Students, Chemists, and Gas Engineers. By W. J. ATKINSON BUTTERFIELD, M.A., F.C.S., Head Chemist, Gas Works, Beckton, London, E. With numerous illustrations. London: Charles Griffin and Co., Ltd. 1896. Pp. 375.

ENGINEERS have so completely possessed themselves of the supreme direction of gas-works that the outside public is apt to forget that we have here to do with an essentially chemical manufacture.

For this reason, among others, we must heartily welcome the appearance of the present work.

Among the numerous points that call for special notice we must mention the increase in the yield of ammonia from coal, effected by an admixture with lime before ignition. The effects of this addition (Cooper's patent) are promised subsequent consideration, but unfortunately we have not been able to meet with the passage.

The effects of high temperature in heating the retorts are duly considered. It is admitted that working at a low temperature yields an improved quality of gas at the expense of its quantity.

It is a serious consideration that the proportion of the deadly carbon monoxide in coal-gas may reach 9 per cent. Hence the possibility of explosions is not the only evil resulting from an escape of gas.

The use of water-gas for domestic purposes requires very great caution, as the proportion of carbon monoxide may reach 33 per cent of the total volume. According to O. Wyss, here quoted from the *Zeitschrift für Angewandte Chemie*, 10 per cent diffused in air renders it fatal to warm-blooded animals, man being included. We see no reference here to the process devised by Mr. Crookes for removing this constituent from water-gas. The Leeds accident cannot be forgotten: how the body of a man poisoned by water-gas was so saturated with carbon monoxide that alarming effects were experienced by the surgeons making the autopsy.

Acetylene, as a material for enriching coal-gas, is not free from objections. Its cost is under many circumstances practically prohibitive, and its toxic properties cannot be overlooked.

The standards of light are of great importance, and involve no small difficulty. The English normal candle, and indeed all normal candles, are untrustworthy. It is found that, however carefully prepared, they cannot be uniformly made to burn exactly 120 grms. of spermaceti hourly. Probably the pentane lamp of A. Vernon Harcourt will be ultimately recognised as the official standard. It emits a light of ten times the value of the standard candle.

The amyl-acetate lamp of F. von Hefner-Alteneck is somewhat similar in principle to the pentane lamp. It has to a considerable extent superseded the German standard paraffin candle. This candle is slightly superior in lighting power to the English normal candle. The German standard paraffin candle = 1.05 English normal spermaceti candle.

The French Carcel lamp is now round exactly equal to ten English normal spermaceti candles.

The standard of M. Violle is the light of a square centimetre of liquid platinum exactly at the solidifying point. It is here pronounced as "deliciously unpractical." The surface of molten platinum is found to have small scum-like particles constantly floating over it, and these particles give far more light than the mass of metal itself.

It is admitted that some large provincial towns, especially in the North, are supplied with a richer gas than in London, as is almost the whole of Scotland. But it is asserted that in the majority of English provincial towns, especially those where the gas works are in the hands of the municipality, the gas is poorer than in London. This charge brought against municipal gas-works is exceedingly improbable, and agrees little with our observations. It is admitted that the tone of the Auer-Welsbach light is unpleasant and greenish.

The heating value of London coal has a power of 155 calories, as against water-gas 72 and Dowson gas 37.

A variety of points connected with lighting-gas, or rather with gas companies, are not touched upon. There is no discussion of the demerits of that "mechanical Ananias," the gas meter. Nor, as we are happy to remark, is their any polemic against the electric light.

Mr. Butterfield, by the production of this book, has laid all concerned under great obligations.

Spiritual Heroes (Guiding Spirits). A collection of Biographies, Edited by D. ANTON BETTELHEIM. Vol. xix., *Darwin, His Life and Activity*, by Professor PREYER, Aulic Counsellor. (Geisteshelden, Herausgegeben von D. Anton Bettelheim. Darwin, sein Leben und Wirken). Berlin: Ernst Hofmann and Co.

THE work before us gives in the brief compass of 208 pages perhaps the most instructive biography of the great reformator of biology which has yet been issued. We notice it with the greater pleasure because its author, Professor Preyer, looks forward hopefully to the extension of the grand principle of evolution to the inorganic world, especially to the chemical elements—referring in this respect to the discourse on the "Genesis of the Elements," delivered by Mr. Crookes in 1887 before the Chemical Section of the British Association—because it throws valuable lights on the origin of genius and on scientific education, and because Darwin, though no chemist, was a careful and successful experimentalist. Had he been placed under slightly different circumstances he might have become an illustrious chemist.

The book opens with a preface by Professor Ernst Haeckel, who speaks of Darwin as "our venerated friend and 'grand master'" ("Altmeister," a term for which we have no exact English equivalent). We come next to an account of Darwin's family, remarkably thorough going and accurate. It is shown to what an extent exceptional intellectual power has prevailed in the family for some generations. The eldest son of Erasmus Darwin (the grandfather of our hero), though he died in his twentieth year from a wound received whilst dissecting, had already given proof of unusual aptitude for the medical sciences. A second son of Erasmus, a genealogist, numismatist, and statistician, died in his 40th year by suicide in an attack of insanity. Francis Galton, a cousin of Charles, is well known for his valuable works on heredity, and Robert Waring Darwin, the father of Charles, was an eminent and successful physician. In short, a study of the career of the Darwin family is a valuable lesson on heredity.

Not less instructive is the next chapter on Darwin's school and university career.

We find that, like Liebig, he was denounced at school as a hopeless dunce, a warning on the folly of estimating youths by their aptitude for the dry stubble of classicism. Neither was he a mathematician, and hence he did not take honours at Cambridge. He derived, however, much benefit from his intimacy with Professor Henslow, who aroused in his mind the latent love for the

study of animal and vegetable nature. He had begun to collect Coleoptera whilst at Edinburgh. The only examination which he "went up for" and passed was that for B.A. at Cambridge, in January, 1831. But in spite of his career at two universities, we may consider him as largely a self-taught thinker and discoverer. He had now escaped several dangers, either of which might have caused him to be lost to science. At Edinburgh he might have become a somewhat dry naturalist, of the school of Professor Jameson. Next, his father wished him to become a clergyman or a physician, but what we must call a fortunate accident intervened. He had the opportunity of joining as naturalist the surveying expedition of the *Beagle* under Captain Fitz Roy. Here he found his true calling, and awoke to systematic and continuous study, and made the observations which ultimately led to his epoch-making work. But for this he had to pay dearly. The *Beagle* was a typical specimen of the ten-gun brigs which then existed in the British navy, and which were notorious for their power of occasioning and intensifying sea-sickness in their crews. From this affliction Darwin suffered all the five years of the expedition, except the short intervals spent on land, and he remained an invalid for the rest of his life. He achieved the wonderful amount of work which he has left us only by the most judicious economy of time and strength.

Professor Preyer's critique of Darwin's theories is of course highly favourable, and is a signal and wholesome contrast to the lamentable comment of M. Blanchard on Lord Salisbury's presidential discourse delivered before the British Association in 1894.

In the account given of the funeral honours paid to Darwin Professor Preyer makes one mistake. The personal attacks on Darwin, and the opposition to the doctrine of evolution, have not ceased, and are indulged in, in France chiefly by the Academy of Sciences, and in England by the "Positivists," whose invectives might, however, be regarded as complimentary.

Exercises in the Preparation of Organic Compounds. By Professor EMIL FISCHER, of Berlin. Translated from the Fourth German Edition by ARCHIBALD KLING, F.I.C. Glasgow: Hodge and Co. London and Edinburgh: Williams and Norgate. 1895. Pp. 80.

It has long been recognised in Germany that as an initiatory training for research the preparation of organic compounds is of the highest value. By such exercises the student learns the arts of manipulation and all the resources necessary for obtaining compounds in the highest state of purity, with the greatest attainable neatness and economy of material and of time, and with the precautions required to avoid dangers. We have here instructions for the preparation of 77 important representative organic substances.

In many instances the characteristic reactions of the product are mentioned as a guide, as also the yield which ought to be obtained. Cuts of the apparatus are given where it has appeared useful. The work has been found exceedingly valuable in the laboratories of several of the German universities, and we hope that Mr. Kling's version will be widely utilised in this country.

An Introduction to the Study of Rocks. British Museum (Natural History), Cromwell Road, London, S.W. Mineral Department. Printed by Order of the Trustees. 1895.

It is to be regretted that the study of mineralogy in the widest sense of the term is far from popular in Britain. Our scientific journals rarely give an account of the discovery or the detailed study of any mineral or rock. This comparative neglect exists in spite of the obvious and

important economic bearings of the question and of the facilities afforded to the student by the collection of the British Museum, even in its present uncentral location. The work before us, which has been drawn up by Mr. L. Fletcher, is enriched with a plan of the mineral gallery at the Museum. The treatment of the subject is clear and simple, and is calculated to be a trustworthy guide to the student. At present we often see, in private collections, a confusion between rocks and mineral species. Some persons who lay claim to no inconsiderable extent of culture deny to a bed of clay or sand the name of a rock or even of a solid. By this error we have known a riparian proprietor who had caused pulverulent matter to be thrown into a stream escape the law concerning the obstruction of streams.

Manual of Metallurgy. (Handbuch der Metallhüttenkunde). By Dr. CARL SCHNABEL, Professor of Metallurgy and Chemical Technology at the Royal Mining Academy of Mines of Clausthal. Vol. I., Copper, Lead, Silver, Gold. With 571 illustrations in the Text. 8vo., pp. 914. Berlin: Julius Springer, 1894.

PROFESSOR SCHNABEL has favoured the technical world with a most elaborate and comprehensive treatise at once theoretical and practical.

Under each metal, *e.g.*, copper, we find a careful account of its physical properties, its chemical attributes, and especially those reactions of the compounds of the metal which are most important for its extraction. Then follows a catalogue of its ores, with their localities, compositions, and percentage of metal.

We then come to its extraction and refining; firstly in the dry way, as applied to copper sulphides, and with different modifications (*e.g.*, pyritic smelting). The author compares the shaft-furnace process, general in Germany and Sweden, with the reverberatory process, common in England, and points out the advantage of the combined process as now in operation both in Germany and England. The Bessemer process for copper may, the author thinks, prove ultimately superior to both.

The various processes are next described in detail with the aid of excellent cuts, for the most part drawn to scale.

The various methods of roasting so as to utilise the sulphurous acid, and to prevent, or at least minimise, the injury produced by its escape into the air, are carefully discussed.

The refining of crude copper is described as performed at Mannfeld, Lake Superior, Pittsburg, Atridaberg, and Oker.

Professor Schnabel then proceeds to the extraction of copper by the wet way, according to the condition in which it occurs.

Concerning the elaboration of copper stones by the electrolytic process, no results have yet been reached which can be pronounced as definitely satisfactory from an economical point of view. With the alloys of copper the results are much more satisfactory.

The metallurgy of lead is next expounded in a similar manner, leading to that of silver. It is to be remarked that the present procedures for the separation of silver from galena fail to give satisfaction, since at the current low prices of silver they are no longer remunerative. Rewards have therefore been offered for some improved method. Electrolysis is here described mainly as applicable to alloys of lead and silver and of zinc and silver. It may, perhaps, not be regarded as an unpardonable digression if we point out that the demonetisation of silver is regarded in some quarters as almost a *casus belli*.

In the section on gold we find that very discrepant statements are made by different authorities concerning its physical properties. Thus its specific gravity is given as 19.30, and again as 20.72. Its conductive power for heat is, according to Despretz, 103 (silver = 100), according to

Calvert and Johnson 98, and according Wiedemann and Franz 60.

At present the author considers that, although the cyanide process for the extraction of gold from ores which contain a large proportion of pyrites and ignoble metals is in many cases applicable, yet in the majority of instances the expense of this process is heavier than that of amalgamation or of chlorination. He recognises, however, that the cyanide process is still in its infancy. It may be that the solubility of gold in a mixture of potassium cyanide with ferricyanide is greater than in cyanide alone.

The present volume of Schnabel's treatise will be found most valuable, and the continuation of the work will prove no less satisfactory.

The Chemistry of Chlorophyll. (Die Chemie des Chlorophyll.) By Dr. L. MARCHLEWSKI. 1895. 8vo., Pp. 82. Hamburg and Leipzig: Leopold Voss.

THIS work, which is dedicated to Dr. Edward Schunck, F.R.S., does not profess to be a complete monograph of the substance in question. It does not enter upon the physiology of leaf-green, its origin in the plant, its vital functions, and its relation to other vegetable products. The other confines himself to the chemical phase of chlorophyll as a green compound capable of dyeing green. It is, however, not a unitary colouring matter, but a mixture of two pigments with a fatty acid. Pure chlorophyll, however, *i.e.*, the substance which has been extracted by alcohol from the green parts of plants, has not yet been isolated. The pure so-called crystallised chlorophyll described in chemical literature consists probably of derivatives of true chlorophyll.

Foremost among such derivatives stands chlorophyll as obtained by the action of weak, especially organic, acids upon chlorophyll. By treatment with stronger acids it is transformed into phylloxanthin and phyllocyanin, which have been recently studied by Schunck. Phyllocyanin, again, by treatment with concentrated acids or by alkalis into phyllotaonin, the best characterised derivative of chlorophyll, is one of the most beautiful substances of organic chemistry.

The original unmodified chlorophyll may be transformed by alkalis into alkachlorophyll, which latter compound, on treatment with acids in presence of alcohol, yields an alkylether of phyllotaonin. On heating phyllotaonin with alkalis at a high temperature we obtain phylloporphyrine.

Each of these products is described in full, with the method of its preparation, its properties, its chemical composition, its spectroscopic behaviour, and its fission products.

We heartily share the author's hope that chlorophyll may soon be as thoroughly treated from the physiological point of view. We feel bound to call particular attention to the admirable bibliography which concludes the work and to the two spectroscopic tables.

CORRESPONDENCE.

ON THE PLACE OF HELIUM IN THE CLASSIFICATION OF ELEMENTS.

To the Editor of the Chemical News.

SIR,—The tone of Mr. Wilde's last letter renders it impossible for me to continue the correspondence with him. I would, however, ask any chemists who are interested in the question of priority which he there raises, to look at the papers mentioned in our letters, and judge for themselves.—I am, &c.,

J. H. GLADSTONE.

17, Pembroke Square, W.,
December 31st, 1895.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Journal für Praktische Chemie.

New Series, Nos. 5, 6, and 7, 1895.

Researches from the Organic Laboratories of the Technical High School at Dresden.—Communicated by E. v. Meyer.—These researches consist of a paper, by P. W. Uhlmann, on the action of cyanacetic ethyl ester upon the salts of mono-nitro-diazobenzene. The author observes that the behaviour of the aqueous solutions of the potassium salts (1 : 300) was interesting. A stratum 10 m.m. in depth, of the three potassium salts absorbed:—The meta-salt; blue and violet entirely. The para-salt; yellow, green, blue and violet completely, orange partially. The ortho-salt; orange, yellow, green, blue, and violet completely. All the three salts were polarimetrically inactive.

On Complex Metallic Bases.—N. Kurnakow.—First Treatise; Chapter II.; a continuation of Metal Salts of the Thioamides. The metal compounds of the thioamides show us distinctly that, in the formation of a complex salt, both the atoms of the metal and the acid residues are simultaneously concerned. The striking stability of the thio-amido-salts of a higher type lead us to the conclusion that in these substances also several mols. of thiamid are directly combined with the metal.

Researches from the Chemical Institute of the University of Erlangen.—M. Busch.—The present treatise—a continuation—is occupied with a study of orthodibenzylamine. It does not admit of useful abridgment.

A Contribution to the Knowledge of the Homologues of Ethylen-diphenolsulphon and Ethylen-ditolylsulphon, with Communications on the Behaviour of Mercaptides with Halogenalkylenes.—R. Otto.—Not adapted for useful abstraction.

The Occurrence of Orthocumaraldehyd methyl Ether in Cassia Oil.—J. Bertram and R. Kursten.—The authors, working in the laboratory of Schimmel and Co., of Leipzig, whilst rectifying a large quantity of the oil of *Cinnamomum cassia*, obtained a crystalline body probably identical with Rockleder's "cassiastearopton." They identify this body with methylorthocumoraldehyd, a compound which they have also obtained synthetically.

A New Manner of the Formation of Secondary Aromatic Amines.—O. Kym.—The author states that his results are very fragmentary and incomplete.

Researches from the Laboratory of the University of Freiburg, in Breisgau.—These researches consist of papers on the "History of Bibromsebacinic Acids," by Ad. Claus, and on "Tautomerism" and "De motropy" by the same chemist. He contends that, if we are not disposed to abandon the entire view of the concatenation of atoms, we must extend it to the assumption that even more than two elemental atoms may unite with a corresponding number of valences in one common combination.

Quantitative Determination of Condensation-Products.—G. Vendt.—The author has exemplified his methods in the cases of the condensation of acetanilide to floraniiline by means of zinc chloride, and that of benzene and chloroform by means of aluminium bromide.

On Experiments for the Production of Carbon Monosulphide.—A. Denninger.—The author's experiments have not led to the results desired. He feels justified in assuming that carbon monosulphide is a liquid boiling at a low temperature, and having a pleasant smell of carbon disulphide. It is readily combustible, and is violently absorbed by alcohol and aniline.

Zeitschrift für Anorganische Chemie,
Vol. ix., Part 1.

Fluorescent Spectrum of Argon, and its Relations to the Aurora Borealis.—M. Berthelot.—See CHEMICAL NEWS, vol. lxxi., p. 212.

A Contribution to the Knowledge of the Copper and Manganese Cyanides.—Paul Straus.—The author describes potassium manganite and manganic cyanides, the double decomposition of these salts with ferric and ferrous salts, the potassium cupromangan-cyanides, and the analogous sodium and ammonium compounds, and the potassium cuprocupri-cyanide.

The Double Haloid Compounds of Cæsium, Rubidium, Sodium, and Lithium with Thallium.—J. H. Pratt.—This paper requires the accompanying figures.

The Volatility of Chromic Anhydride.—Henryk Arctowski.—This anhydride is volatile far below its melting-point.

Synthesis of some Ore-minerals and Analogous Metallic Compounds by their Solution and Crystallisation in Fused Metals.—Fried. Rössler.—This memoir requires the accompanying 34 figures.

A Preliminary Communication.—Carl Engels.—With reference to the remark of P. Jannasch, that he is about to undertake the electrolytic separation of metals with the simultaneous presence of organic substances and hydrogen peroxide, the author mentions that he has been engaged for a considerable time with experiments in this direction.

Vol. ix., Parts 2 and 3.

Quantitative Determination of Lead.—A. Kreichgauer.—This voluminous memoir requires the accompanying figures. The author's method is electrolytic. It is pointed out that the platinum capsules serving as electrodes should be *turned*, not hammered.

On the Ferrocyanides.—J. Messner.—An examination of Turnbull's blue, of Berlin green, and of Williamson's violet. The individuality of the last-mentioned substance is regarded as questionable.

Experiments for the Production of Pure Zinc.—F. Mylius and O. Fromon.—This paper cannot be reproduced in full without the insertion of the seven accompanying figures. The principal results are that the so-called pure zinc of commerce always contains determinable quantities of cadmium, lead, and iron. Solution of zinc sulphate can be so effectually purified electrolytically that in its chemical analysis we cannot detect any foreign heavy metals. Zinc oxide can easily be obtained chemically in corresponding purity. The electrolytic zinc obtained from zinc sulphate or oxide contains recognisable quantities of platinum derived from the anode. The purest zinc is obtained by repeatedly refining the metal electrolytically in basic solutions of zinc sulphate. The product is spongy, and requires to be re-melted and sublimed *in vacuo*. The metal thus obtained contains at least 99.999 per cent of zinc. In the electrolytic separation of zinc from solutions, the secondary decomposition of water cannot be entirely avoided. The formation of zinc-sponge takes place with the co-operation of oxygen.

The Separation of Metals in a Current of Carbonic Acid charged with Bromine.—P. Jannasch and E. Rose.—The authors describe here the separation of bismuth and cobalt, of bismuth and nickel, of tin and antimony, from lead and copper. The authors' methods cannot be described intelligibly without the three accompanying figures.

Specific Heat of Hydrogen Peroxide.—W. Spreng.—The facts ascertained show accordingly the imperfect consumption in the compound H_2O_2 of the potential chemical energy of the elements H_2 and O_2 . On the other hand, they demonstrate the theorem of De Heen,

according to which the variation of the specific heat of liquids depends on dissociation.

The Action of Ferric Chloride upon Metallic Iodides.—Karl Seubert and Karl Gaab.—A complete abstraction of this memoir would require the insertion of the five tables of curves. In general it may be said that the influence of the metal present as iodide upon the course of the reaction is for the most part insignificant, and always much smaller than that of the acid contained in the ferric salt. In the latter case the presence of sulphuric acid, in place of hydrochloric acid, determines a decrease of the free iodine to the extent of more than 20 per cent of the theoretical quantity. With ferric acetate alone no iodine is liberated.

MISCELLANEOUS.

The Leather Industries.—We are informed that a course of lectures with experimental demonstrations will be given by H. R. Procter, F.I.S., at the Yorkshire College, Leeds, on "Recent Processes in Leather Manufacture." The course will commence on Wednesday, January 15th, 1896. We consider that this course merits the support of all persons connected with the leather trades, not alone from the well-known ability and experience of the lecturer, but because the authorities of the Yorkshire College rightly consider it of the first importance that their lecturers should teach by their own syllabuses and not by those of an extraneous body. By insisting on this principle they deserve the gratitude of all friends of British industry.

On a Possible Procedure for Separating Atmospheric Argon or Nitrogen.—Claudius Linb.—One of the best procedures for separating argon from atmospheric nitrogen consists in absorbing the latter by means of lithium. Unfortunately this metal is very rare, and the lithium thus obtained has consequently an excessive price. I have indicated that simple barium fluoride or barium and sodium double fluoride treated with sodium at a moderate heat yield a grey substance, evidently reduced barium, which absorbs the nitrogen of the air energetically. It would be easy to make this preparation in a stout iron tube, which would then serve for the passage of atmospheric air, previously deprived of its watery vapour, its carbonic acid, and its oxygen. The price of sodium and of the fluoride, double or single, prepared as I have indicated, being low, we might have argon relatively cheap. The procedure, always supposes that argon resists this absorbent; if the contrary is the case the fact will still be interesting. I purpose to experiment on this process and determine with precision the physical and chemical properties of this gas.—*Comptes Rendus*, cxxi., p. 887.

MEETINGS FOR THE WEEK.

MONDAY, 13th.—Medical, 8.30.

TUESDAY, 14th.—Institute of Civil Engineers, 8.

— Photographic, 8.

— Royal Medical and Chirurgical, 8.30.

— Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.

WEDNESDAY, 15th.—Society of Arts, 8.

— Meteorological, 8. (Anniversary).

— Microscopical, 8. (Anniversary).

THURSDAY, 16th.—Royal Institution, 3. "Dante," by Philip H. Wicksteed, M.A.

— Royal, 4.30.

— Royal Society Club, 6.30.

— Institute of Electrical Engineers, 6.30.

— Chemical, 8. "The Acetylene Theory of the Luminosity of Hydrocarbon Flames," by Prof. Vivian B. Lewes. And other papers.

FRIDAY, 17th.—Quekett Club, 8.

— Royal Institution, 3. "More about Argon," by The Right Hon. Lord Rayleigh, F.R.S.

SATURDAY, 18th.—Royal Institution, 3. "To the North of Lake Rudolf and among the Gallas," by Dr. A. Donaldson Smith, F.R.G.S.

THE CHEMICAL NEWS.

VOL. LXXIII., No. 1886.

NOTE ON THE RAPID ESTIMATION OF INSOLUBLE PHOSPHATE.

By VINCENT EDWARDS, F.C.S.

THERE can be no doubt that the estimation of both "soluble" and "insoluble" phosphates in manures is best effected by weight, but at times, when results are required without delay, the volumetric method by means of uranium acetate is extremely useful, and with precautions good results can be obtained, especially with superphosphates and dissolved guanos. This applies, however, more to the "soluble" determination than the "insoluble." In the latter case various substances become dissolved and render the end-reaction with ferrocyanide obscure, and the results therefore untrustworthy. Though I would certainly not advocate the substitution of any volumetric process for the usual gravimetric one, I made a few experiments to ascertain, as a matter of interest, the most suitable conditions under which the "insoluble" phosphate in manures can be estimated by titration with solution of uranium acetate, and venture to submit as the most satisfactory the following:—

I take a small quantity of the well mixed sample, about 0.5 grm., and exhaust with cold and hot water, collect the undissolved matter as usual on a small Swedish filter-paper, and washing till the filtrate coming through is no longer acid. The residue is then washed off the filter-paper with hot water into a small beaker, and treated with a very small quantity of HCl and boiled on a sand-bath for a short time. The hot solution is then run through the same filter into a larger beaker, the sand washed, and the filtrate diluted to 300 c.c., ammonia added till alkaline, and afterwards acetic acid till just acid. The smaller the amount of HCINH_3HO and $\text{HC}_2\text{H}_3\text{O}_2$ employed the better. The beaker is then placed on a sand-bath, heated till warm, and a few drops of uranium acetate run in, and the heating continued till the usual precipitate appears; the titration is then carefully finished, a deep colour being taken as the end-mark. The results by this method may be a trifle low, but with care will be found very near those by weight. The dilution greatly increases the accuracy of the method, and it is possible that a weaker solution of uranium might be also used with advantage for the "insolubles" than the ordinary one (1 c.c. = 0.01 grm. $\text{Ca}_3\text{P}_2\text{O}_8$), and I intend to try some experiments on this point.

Work's chemists, who are often called on to furnish rapid results for home use, will do well to try this plan. I need scarcely say the uranium must be standardised under the same conditions as the titrations are made.

Lawes' Works, Barking, Essex,
January 1, 1896.

THE CHLORIDES OF ZIRCONIUM.

By F. P. VENABLES.

IN a report upon the examination of the chlorides of zirconium (*Journ. Amer. Chem. Soc.*, 1894, xvi., 460-475) it was stated that pure zirconium tetrachloride was formed by the solution of zirconium hydroxide in hydrochloric acid and repeated crystallisation from the concentrated acid. This statement was based on a partial analysis by Linnemann (*CHEMICAL NEWS*, lii., 233-240), the result of which made him call the substance the

tetrachloride; and on repeated partial analyses of my own, in which the zirconium present was determined by ignition as zirconium dioxide. So firmly convinced was I of the fact that this was the normal tetrachloride that I determined to use it in revising the atomic weight. Ten closely agreeing determinations were made, and they yielded, as the percentage of zirconium dioxide found, 52.99, or, calculating with 90.62 as atomic weight of zirconium (Bailey), 39.16 per cent of zirconium. The zirconium in the tetrachloride amounts to 38.99 per cent.

Bailey made several very widely differing determinations of the chlorine in this body, and considered it the oxychloride. His determinations varied so greatly, and his mode of drying was so faulty, that I simply concluded he was mistaken, being unable to detect a source of error in my analyses which would allow for a change from 39.16 per cent of zirconium to 46.79 per cent, the amount needed for the oxychloride.

Still, as a necessary precaution, I made some determinations of the chlorine in the pure crystalline product, and was greatly surprised to find only 35.5 per cent of chlorine instead of 61.01, the amount required for the tetrachloride. The percentage in the oxychloride would be 36.63.

I regard the results as very singular. The substance must be an oxychloride, but what is its composition? The simplicity of its preparation, and the constancy of its composition along with its stability, would argue for a simple formula. No such formula can be calculated from the analysis. Probably the best formula suggested for this oxychloride, corresponding closely with the above analysis, is $\text{Zr}_3(\text{OH})_5\text{Cl}_7 \cdot 5\text{H}_2\text{O}$. — *Journ. Amer. Chem. Soc.*, vol. xvii., p. 842.

ON THE ANALYSIS OF ALLOYS OF LEAD, TIN, ANTIMONY, AND ARSENIC.

By LAUNCELOT ANDREWS.

THE experiments described in the present paper were carried out under my direction, during the last winter, by Mr. Earl Durfee. Part of them were suggested by Drown's investigation of the separation of tin from lead by repeated evaporations with concentrated hydrochloric acid, but were carried out previous to the publications of Jannasch (*Ber. d. Chem. Ges.*, xxvii., 3335), and of Jannasch and Schmitt (*Zeitsch. Anal. Chem.*, ix., 274) on the same subject. All experiments referred to here relate to the analysis of an alloy containing in round numbers 80 per cent lead, 13 per cent antimony, 7 per cent tin. The exact composition of this metal will be given later.

First Method.

The attempt was made to drive off all tin and antimony as chlorides, according to Drown. To this end 1 grm. of the alloy was dissolved in aqua regia and evaporated to dryness, heating the residue to 200° C. The latter was moistened with about 4 c.c. fuming hydrochloric acid, and evaporated as before, the whole operation being repeated five times. The remaining lead chloride was, however, not free from tin and antimony. A series of attempts were then made to effect a separation by treating the alloy with bromine and hydrochloric acid gas, in varying forms of apparatus and at various temperatures. The details of these experiments need not be given, since they either failed to give a complete separation or were affected by practical faults of one kind or another.

On the other hand, no difficulty was found in completely volatilising all the tin and antimony by heating the alloy directly, without previous solution, in a current of hydrochloric acid gas which had passed through concentrated nitric acid. The process was carried out as

follows:—Hydrochloric acid gas, evolved in a slow and steady stream by allowing the fuming acid to flow through a capillary tube into concentrated sulphuric acid, passes first through a flask containing 10 c.c. of nitric acid of 1.50 sp. gr., and then through a combustion-tube of large diameter, 30 c.m. long, containing a porcelain boat with the alloy in the form of turnings. The current of gas on leaving the combustion-tube traverses a Volhard absorption flask, charged with a solution of potassium bromide and kept cold during the process. The combustion-tube is covered with an asbestos tent, and heated, by means of an Argand burner, to 210° C. The amount of the alloy used in each experiment was a half gram., and in two hours—during which time the operation required no attention whatever—the separation was complete, and the snow-white residue in the boat was completely soluble in boiling water, while the distillate in the receiver was free from lead. The lead was weighed as sulphate. The receiver contained the antimony and tin and a little arsenic. To it was added the solution obtained by rinsing the unheated part of the combustion-tube with hydrochloric acid. The small amount of arsenic present was easily separated from the contents of the receiver by distillation according to Gooch and Phelps (*Zeitsch. Anal. Chem.*, vii., 123). After the removal of the arsenic, tin and antimony were separated by Carnot's method (*Zeits. Anal. Chem.*, lxxxviii., 650), which was found to be excellent.*

The process as described may be modified by attacking the alloy with nitric acid first, in a two-necked flask, then evaporating in a current of hydrochloric acid gas and heating in the same as before. The quantitative results are concordant, but the modified process is less convenient and requires decidedly more time.

Analytical Results.

	I. Grm.	II. Grm.	III. Per cent.	IV. Per cent.
Alloy taken	0.5000	0.5000	—	—
Lead sulphate	0.5849	0.5853	—	—
Lead found	0.3988	0.3991	79.75	79.82
Antimony trisulphide..	0.0925	0.0925	—	—
Antimony found.. ..	0.0661	0.0661	13.21	13.21
Stannic oxide	0.0434	0.0437	—	—
Tin found	0.0342	0.0344	6.84	6.88
Arsenic (volumetrically)	0.0006	0.0007	0.12	0.14
Total			99.92	100.05

Second Method.

It has been observed that, when various kinds of anti-friction metal or type metal were boiled with hydrobromic acid or with mixtures of hydrochloric acid and potassium bromide, the antimony remained undissolved, the arsenic distilled off, and all the other constituents of the alloy went into solution. A more critical examination of the matter showed that, under the conditions named, in the presence of air, a small amount of the antimony dissolved, but that the undissolved portion was free from lead and tin. On the theory that the partial solution of the antimony was due to the oxidising action of the air, it seemed likely that the addition of a powerful reducing agent, such as hydriodic acid, would prevent the loss of antimony, a view which was confirmed by an experiment in which potassium iodide took the place of the bromide.

One gram. of the metal, in turnings, after boiling for one hour with hydrochloric acid of 1.10 sp. gr. and potassium iodide (about 1 gram.) was entirely disintegrated. The antimony remained undissolved as a dark grey powder. It was filtered from the boiling solution through a Gooch

filter, washed with boiling water until free from lead iodide, dried, mixed with sulphur, and gently ignited in a stream of carbon dioxide. This conversion into sulphide is needful because the finely divided antimony obstinately retains either water or hydrogen, in consequence of which the results come about seven-tenths per cent too high if the metal is weighed directly.

Analytical Results.

	I.	II.
Metal taken	1.0000	1.0000 gm.
Antimony weighed direct	0.1385	0.1375
Antimony trisulphide ..	0.1827	0.1833
Antimony calculated ..	0.1305	0.1310
Antimony.. ..	13.05	13.10 per cent.

The subjoined table presents a summary of the results obtained by the different methods of analysis of the same alloy. Column I. gives the results obtained by tedious but exact methods, not described in this paper but employed for a control. Column II. gives the figures obtained by the first method above described. Column III. those of the second method. Column IV. the mean of all of the results.

Summary.

	I. Per cent.	II. Per cent.	III. Per cent.	Mean. Per cent.
Arsenic..	0.13-0.12	0.12	0.14-0.13	0.128
Antimony	13.13-13.15	13.21-13.21	13.05-13.10	13.14
Tin ..	6.83-6.84	6.84-6.88	—	6.85
Lead ..	79.87-79.95	79.75-79.82	—	79.85
Total				99.97

In conclusion, I wish to draw attention to a convenient device for maintaining temperatures lying between 200° and 500°, which are difficult to secure with certainty by means of a Bunsen, or even in some cases by the ordinary forms of air-bath. The device consists simply of an ordinary Argand gas-burner with chimney, as made for illuminating purposes, with the addition of a simple hood or tent of asbestos and sheet-iron to go over the top of the chimney and confine the heat. It is surprising what a wide range of temperatures this simple apparatus gives command of. It is very perfectly adapted for the ignition of antimonous sulphide in carbon dioxide, an operation which can be carried out with great nicety at 400°, but which is difficult and uncertain when a Bunsen burner is used as the source of heat. Many other operations, distillations, digestions, &c., are carried on advantageously in this way, the great merit of the arrangement consisting in the superior control of the temperature. It is, for example, well adapted to the conversion of calcium oxalate into carbonate. — *Journ. Amer. Chem. Soc.*, vol. xvii., p. 869.

ON THE CONSTITUTION OF WATER AND THE CAUSE OF ITS DISSOCIATIVE POWER.

By J. W. BRÜHL.

IN the aqueous solutions of salts of strong acids and bases the observed alteration of the freezing- and boiling-points is known to be approximately twice as great as it ought to be normally, and according to the original equation of van't Hoff. We know, likewise, that this apparent abnormality has been removed by Arrhenius, who showed that all substances which behave in this manner in aqueous solutions are electrolytes, the dissociation of which into ions must have the above behaviour as a consequence.

It is, further, known that many kinds of organic bodies in certain solvents form double molecules or larger mole

* In this method the solution, containing an oxalate and free oxalic acid and much ammonium chloride, is boiled with sodium thiosulphate. Beside the precautions given by the originator of the method, it is essential to success that the solution be boiled violently until one-fourth is boiled away, and that, finally, the acid be in excess as regards thiosulphate.

cular complexes. This is especially the behaviour of the fatty acids, the oximes, the alcohols, &c., when dissolved in hydrocarbons, in chloroform, or in carbon disulphide. On the other hand, the complex molecules are broken up when such bodies are dissolved in water. Alcohols, ethers, esters, ketones, phenols act likewise as dissociative media, though less completely. These latter organic solvents prove also to a certain degree ionising agents, as, *e.g.*, it appears that when saturated with hydrochloric acid gas they have a greater or less conductivity, whilst solutions of hydrochloric acid in benzene or other hydrocarbons have little or no conductive power.

It is not yet sufficiently explained how the dissociating action of the above-named solvents arises, and especially why, in this respect, water by far surpasses all known substances.

The tetravalence of oxygen was rendered probable by Ch. Friedel twenty years ago, and has been confirmed by the author's researches on hydrogen peroxide. If hydrogen peroxide has the constitution $\text{H} \cdot \text{O} : \text{O} \cdot \text{H}$, the formula of water must be—



i.e., it must be regarded as a non-saturated compound. In fact, of all known substances, none displays the criteria of non-saturation in so striking a degree as water. Nearly all bodies have the tendency to combine with it, *i.e.*, they are hygroscopic; there exist numberless hydrates and compounds with crystalline water; and, finally, water is the most universal solvent. All this argues unanimously for the presence of unexhausted affinities, which is satisfactorily explained by the formula



The supplementary valences of the tetravalent oxygen are evidently the cause of the power of splitting off ions, and of the dissociative power of water which is brought into play, as against molecular aggregates. These same supplementary valences are the focus of the creative power by means of which water plays so weighty a part in the household of nature.

This theorem receives further and very essential support in the fact that all those organic solvents which are known as good dissociating media, *i.e.*, the alcohols, ethers, esters, ketones, phenols, urethan, &c., contain oxygen, whilst the non-dissociative or feebly dissociative media, such as the hydrocarbons, carbon disulphide, chloroform, carbon chloride, are all free from oxygen. Further, the substances especially capable of association, such as the carbon acids, the alcohols, and oximes, are oxygen compounds, and that water, in particular, forms complex molecular aggregations.

From all these considerations we may regard it as established that it is the presence of water, principally if not exclusively, which determines the tendency of the above-mentioned substances to form complex molecules, and also occasions the dissociating force. Water has the greatest proportion of oxygen and the greatest dissociative power; then follows in this respect, among the alcohols, in the first place, methylic alcohol, whilst its higher homologues decrease more and more in capacity for association and in dissociative power. The competition for the atom of oxygen becomes the stronger the more other kinds of atoms are present in a molecule, and the more completely its tendency to combination is satisfied.

Hydrogen peroxide is very much richer in oxygen than is water. In this substance, that tendency of the hydrogen atoms to combination is gratified only to a small extent. Further, the so-called triple bands of the molecule, $\text{H}-\text{O}\equiv\text{O}-\text{H}$, may be resolved, and hence hydrogen peroxide may be regarded as a highly non-saturated body—to a greater extent than water. The conjecture is forced upon us that hydrogen peroxide must possess a great dissociative power, probably still greater than that of

water. This cannot be readily shown in a direct manner by the electrolysis of dissolved bodies, or by cryoscopic and ebullioscopic determinations, on account of the instability of hydrogen peroxide. But it will be possible in an indirect manner.—*Comptes Rendus*, cxxi., p. 2866.

THREE NEW REAGENTS FOR NITRITES.

By G. DENIGÈS.

AMONG Griess's reagents, which are being more and more used for the detection of nitrous acid, the salts of meta-phenyldiamine are especially admired. Along with their excellent properties, they possess various defects, *e.g.*, they are attacked by the halogens, by hypochlorites, and hypobromites, and their solutions are readily decomposed by air. The author recommends the following reagents which are, in part at least, free from these defects:—

1. Phenol, if boiled with Millon's reagent, gives a precipitate which dissolves in acetic acid with a red colour. This reaction renders it possible to detect phenol at a dilution of 1 : 2,000,000. Millon's reagent is a solution of mercury nitrite and nitrate; the effective substance being the mercurous nitrite or nitrous acid in presence of a mercurous salt. Hence, for the detection of nitrous acid the author uses the following solutions:—(a) Phenol, 1 grm.; sulphurous acid, 4 c.c.; water, 100 c.c. (b) Mercuric oxide, 3.5 grms.; glacial acetic acid, 20 c.c. water are mixed; $\frac{1}{2}$ c.c. of sulphuric acid is added, and the mixture is filtered. For use, equal volumes of *a* and *b* are mixed, heated to ebullition, when 1 or 2 drops of the solution in question are added. If 0.5 grm. nitrite is present in 1 litre of liquid a red colouration appears.

2. 2 c.c. aniline are dissolved in 40 c.c. glacial acetic acid and made up with water to 100 c.c. Of this solution, 5 c.c. are boiled with a corresponding quantity of the liquid in question. (In very concentrated solutions 1 drop is sufficient). In presence of nitrous acid there appears a straw-yellow or a deep orange-colour, which on cautious acidulation passes into a red. Chlorates and nitrates do not interfere as do hypochlorites, hypobromites, free chlorine, and bromine. An excess of acid may interfere, whence strongly acid liquids should be previously neutralised.

3. Resorcin, 1 grm.; water, 100 grms.; sulphuric acid, 10 drops. Place in a test-tube 10 drops of the liquid to be tested, 2 c.c. of pure sulphuric acid, 5 drops solution of resorcin, and shake up. The presence of nitrous acid produces a carmine-red or violet-blue solution, which is very intense at 0.01 m.grm.—*Journal de Pharmacie* and *Chemiker Zeitung*.

THE

TOXICOLOGICAL DETECTION OF AQUA REGIA.

By P. MOLA.

THE author has established by experiments on meat mixed with aqua regia (100 grms. meat, 500 grms. water, and 2 c.c. aqua regia) that, at common temperatures, the mixture does not evolve the slightest traces of chlorine or hydrochloric acid, but traces of nitrous acid. If such a mixture is submitted to fractional distillation, raising the temperature gradually to 140° and 170°, we always obtain neutral distillates, and a faint acid reaction is obtained only on raising the temperature to 190°. In these distillates traces of nitrous acid may be recognised, but not of nitric or hydrochloric acid. The residual substance has a strongly acid reaction, depending on the formation of acid albumens. Distillation is therefore useless for the detection of aqua regia in organic matter. The best pro-

cess is that proposed by Vitali for the detection of hydrochloric acid. The substance in question is heated in a porcelain dish to 50–60°, and gradually mixed with small portions of finely pulverised quinidine until the acid reaction has disappeared. The liquid portion in which the two acids are present as quinidine hydrochlorate or nitrate is filtered off; the filtrate is concentrated and mixed in a large glass tube with two-thirds of its volume of chloroform. To this mixture alcohol is added sufficient to dissolve the chloroform, which is then again eliminated by the addition of water. Both the quinidine salts remain dissolved in the chloroform, the solution is filtered through a double filter, the chloroform is evaporated off, and the residue is taken up in hot water. In this solution nitric and hydrochloric acids can both be detected by their reactions.—*Boll. Chim. Farmac. and Chemiker Zeitung*.

ON THE COLOUR OF THE IONS AS A FUNCTION OF THE ATOMIC WEIGHTS.

By JULIUS THOMSEN.

THE *Zeitschrift für Anorganische Chemie*, vol. x., p. 153, contains a treatise by Carey Lea "On the Relation of the Colours of Atom, Ion, and Molecule."

In it the author arrives at the conclusion that the received periodic system appears non-acceptable as being built upon erroneous principles, and proposes in its stead another form, founded upon the colour of the ions. But the dependence of the colour of the ions upon the atomic weight appears quite simple if we use the form of the periodic system which I have published (*Zeit. Anorg. Chemie*, ix., p. 192). The dependence can then be simply expressed by the following words:—"Only the ions of the mean numbers of the greater series are coloured." The two first series, each with seven members, contain no coloured ions; the two next, with seventeen members each, contain in each series seven to eight coloured ions from titanium to copper, and from niobium to silver; and in the fifth series, with thirty-one members, some of which are as yet undiscovered, we also find in its middle the groups of coloured ions (from cerium to gold); whilst in all the series colourless ions correspond to the extreme members.—*Zeit. für Anorganische Chemie*, x., p. 153.

CONTRIBUTIONS TO THE SEPARATION OF MERCURY FROM THE METALS OF THE ARSENIC AND COPPER GROUP.*

By CARL VON USLAR.

POLSTORFF and Bülow have shown that mercury can be very sharply and conveniently separated from lead, silver, bismuth, and copper, as also from arsenic and antimony, by treating their sulphides with a mixed solution of potassium sulphide and hydroxide.

The sulphides of the four former methods are then left entirely undissolved, whilst mercury sulphide passes into solution along with arsenic and antimony sulphides. From this solution mercury sulphide can be separated quantitatively by the addition of ammonium chloride, whilst arsenic and antimony remain entirely in solution.

This method is found useless for the separation of mercury and from tin. In presence of cadmium sulphide mercury sulphide is very imperfectly dissolved by the mixture of potassium sulphide and hydroxide, and from the solution of tin disulphide and mercury sulphide in the above mixture tin sulphide is always separated along with

mercury sulphide in considerable quantity on treatment with ammonium chloride, whilst at the same time a part of the mercury sulphide remains in solution along with the rest of the tin sulphide.

Polstorff has attempted to separate mercury from the metals of the copper and arsenic group by H. Rose's method, *i.e.*, by separation as mercurous chloride by means of phosphorous acid.

Rose has shown that mercury can be quantitatively separated from single metals of this group by means of phosphorous acid, in presence of all the metals in question. Polstorff has hitherto found the separation impracticable.

In my experiments here described I have used the same metallic compounds employed by Bülow, prepared and tested as described in his dissertation. But I preferred using pure copper oxide in place of copper sulphate.

For the separation of mercury I used a phosphorous acid obtained in the known manner by the deliquescence of phosphorus exposed to the air.

The phosphorous acid thus obtained certainly contains some arsenious acid, but, as direct experiments, show so little that the presence of this impurity occasions no inconvenience even in the separation of mercury from arsenic and antimony.

In order the better to measure off the phosphorous acid for the several experiments, the syrupy acid was diluted with four parts of water by weight. Of this syrup—at about 20 per cent—about 5 c.c. were used to 0.1 grm. of mercury chloride. The separation of the mercurous chloride was effected at a temperature of about 40°. It did not seem advisable to separate the mercury at the ordinary temperature, since it would then be necessary for the mixture to stand for ten to twelve hours, and on prolonged standing in the cold, as also in the presence of free mineral acids, there easily ensues a separation of phosphites or phosphates of the metals of the copper group. The separations were effected simultaneously in hydrochloric and nitric solutions in order to decide whether the presence of either of these acids is more favourable to the separation than that of the other.

The separations in hydrochloric solution were carried out in duplicate, in one with a smaller, and in the other with a larger addition of hydrochloric acid, and in all the separations about equal quantities of liquid (150 c.c.) were used. The mercurous chloride was not directly weighed as such, since in its separation in heat a further reduction to metal readily takes place. It was found this reduction to metal ensues especially readily in presence of much hydrochloric acid, whilst it was not observed in nitric solutions. It appeared also desirable to test the mercurous chloride liberated as to its purity, *i.e.*, to determine whether it is quite free from compounds of the other metal from which it had to be separated. This examination in the case of all metals except cadmium and tin can be effected readily and without loss by the method elaborated by Polstorff and Bülow.

In order to escape needless repetitions in describing the various separations, I will here describe the procedure adopted.

The solution of the metallic compounds mixed with the quantities of acid stated in the several experiments was diluted to 150 c.c. heated to 40–45°, and the phosphorous acid was then added. It was then allowed to stand at the most uniform temperature from five to six hours, with frequent stirring. The precipitate was then collected and thoroughly washed with highly diluted hydrochloric acid or nitric acid. The filtrate was mixed as a check with a few c.c. of the solution of phosphorous acid and allowed to stand for some hours at a temperature of about 40°. If a further separation took place it was collected, well washed, and added to the former precipitate. From the filtrate the metal was separated in a suitable manner as indicated in the several experiments, and weighed. The filter, or otherwise the two filters, with the precipitate of mercurous chloride was placed in a beaker mixed with

* *Zeitschrift für Analytische Chemie*, vol. xxxiv., p. 391.

potassium chlorate (0.5 grm.) and hydrochloric acid (25 per cent), allowed to stand in the cold for some hours, and was then heated on the water-bath with a little water until the odour of chlorine had completely disappeared. It was then filtered, the residues of the filter were washed with hot water containing hydrochloric acid, and the filtrate was heated on the water-bath and precipitated with hydrogen sulphide. The precipitate was collected, rinsed back from the perforated filter into the beaker with hot water containing potassium sulphide, and digested with the mixed solution of potassium sulphide and potassium hydroxide. If there remained a slight residue—which was the case only in the separation of mercury from bismuth and lead—it was collected and united to the bulk of the metal in question. From the solution the mercury was separated as a sulphide by heating with sal-ammoniac, the sulphide was again dissolved in hydrochloric acid and potassium chlorate, the solution perfectly free from chlorine was precipitated with hydrogen sulphide, observing the conditions specified by Polstorff and Bülow, the mercury sulphide collected on a weighed filter, and dried until the weight remained constant. After weighing I convinced myself each time of the purity of the mercury sulphide by incinerating the filter and precipitate in a weighed porcelain crucible.

My researches had in the first place the purpose of ascertaining a method which should permit us to separate mercury from the metals of the arsenic and copper group, if all the frequently occurring metals of this group are present. But as the salts of several metals of this group are soluble in water without decomposition only in presence of considerable quantities of free acid, it was necessary to use rather strong acid solutions for such separations. There were hitherto no accounts of the influence of considerable quantities of free acids on the precipitation of mercury as chloride by phosphorous acid.

H. Rose merely states that in precipitating mercurous chloride it is necessary to operate in an acid solution, but he does not give the quantities of acid which must be added for the precipitations. In the text-books of quantitative analysis, by Fresenius and Finkener, we find it merely laid down that a strong dilution is necessary in presence of nitric acid. It seemed hence important to determine whether the precipitation of mercurous chloride by Rose's method is affected by the presence of considerable quantities of hydrochloric or nitric acid. To this end the following experiments were performed.

(a) Taken, 15 c.c. hydrochloric acid and the same weight of phosphorous acid. The liquid was allowed to stand for four hours at a temperature of 40°. The mercurous chloride was entirely precipitated, but its grey colour indicated a partial reduction to the state of metal.

(b) Taken, 20 c.c. nitric acid (of 25 per cent). The mercurous chloride was snow-white, so that no reduction to metal was recognised.

In both experiments the method above described was adopted and the mercury was determined as sulphide.

Here, as in subsequent separations, it was manifest that a reduction to the state of metal does not ensue in a nitric solution, whilst in hydrochloric solutions the reduction frequently goes on to the metallic state, especially if the quantity of acid is large. Hence the separations, if at all possible, should be effected in a nitric solution, as in case of a reduction to metal volatilisation is very possible.

Separation of Mercury from Copper.

In all experiments the copper was weighed out as oxide. In order to obtain pure copper oxide, a hot solution of perfectly pure copper sulphate was poured in an excess of a boiling solution of soda in a large platinum capsule. The precipitate was washed in the platinum capsule until the sulphuric acid reaction disappeared, dried, and slightly ignited. The precipitate was then heated for some time in the capsule with solution of soda, in order to decompose any possible traces of basic sulphate; thoroughly washed, dried, and slightly heated.

The cupric oxide was now found quite pure, and its purity was then analytically demonstrated.

Before proceeding to separate the mercury from the copper, I satisfied myself, by qualitative experiments, that phosphorous acid on being allowed to act for eight hours at the temperature of 40° occasioned no separation of copper phosphate or phosphite. The experiments proved that the separation of mercury from copper can be effected smoothly by means of phosphorous acid in presence of either hydrochloric or nitric acid.

Separation of Mercury from Cadmium.

The cadmium was weighed as oxide. Before weighing the cadmium oxide was ignited and then allowed to cool in the exsiccator. The separation was effected both in hydrochloric and in nitric solutions.

In the separation of mercury from cadmium, an examination of the separated mercurous chloride for the presence of occluded cadmium compounds, according to the potassium-sulphide-hydroxide method, was excluded, since, as the experiments of Bülow have shown, this method does not admit of a smooth separation of the two metals.

Hence the mercurous chloride was converted into mercuric chloride by digestion with hydrochloric acid and potassium chlorate, and the solution of the latter after the free chlorine had been completely expelled by heat, was directly precipitated with hydrogen sulphide. On subsequently testing the weighed precipitate of mercury sulphide, it was found completely volatile, and therefore contained no admixture of cadmium.

The re examination of the filtrates with phosphorous acid proved that a digestion for five hours is sufficient for the complete elimination of the mercurous chloride. The presence of an excess of hydrochloric acid (about 5 per cent) occasioned a partial reduction of the mercurous chloride to the state of metal. If nitric acid is used the precipitate is snow-white.

In the filtrate from the mercurous chloride, the cadmium is thrown down as sulphide; the sulphide is dissolved in hydrochloric acid with the addition of a small quantity of potassium chlorate. From the solution the cadmium is precipitated as a carbonate at a boiling temperature by sodium carbonate, avoiding excess. The liquid is then kept for some time in ebullition, filtered whilst still boiling, washed with boiling water, the precipitate is dried, and the dried precipitate after being separated as completely as possible from the filter is placed upon glazed paper. The remnants of the precipitate still adhering to the filter are dissolved in hot dilute nitric acid, the solution is evaporated to dryness in a weighed porcelain crucible on the water-bath, and gently ignited. When cold, the bulk of the precipitate is added to the residue and heated, at first gently and then strongly, until the weight is constant.

(To be continued).

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 17.)

CHAPTER IV.

CHEMICAL RESEARCHES ON CARBONATE, SULPHATE, AND CHLORIDE OF LITHIUM.

WHEN undertaking my researches on lithium, my principal object was to ascertain whether the carbonate of this metal, prepared in different manners, could be reduced to a state always identical with itself. These researches have enabled me to show that the method pointed out by M. L. Troost, which consists in dissolving the carbonate

of lithium in water containing carbonic acid, to eliminate the greater part of the sodium, attains that end most rapidly; and that the use of sesqui-carbonate of ammonium, to precipitate this compound of lithium, is the only one to be recommended. I learnt, moreover, that the precipitation of the salts of lithium by carbonate of ammonium ought to be performed in platinum vessels. If it is done in glass, as I used to do it *unwittingly*, silica, lime, and sodium are introduced from the glass. Glass is rapidly attacked by sesqui-carbonate of ammonium. I have found that a Bohemian glass beaker lost 0.023 grm. in weight during the time necessary to raise half a litre of very slightly ammoniated water from 15° to 100°, and that, in this case, it added 0.011 grm. of silica to the ferric hydrate made in this ammoniated water.*

These researches demonstrate that oxalate of ammonium does not entirely precipitate the calcium contained in a concentrated solution of nitrate of lithium, and also that sulphate of ammonium is not able to eliminate a salt or hydrate of barium in solution, from this nitrate.

Lastly,—a less-known fact.—absolute alcohol, when mixed with twice its volume of ether, dissolves in salts of barium, remaining in either melted or dissolved nitrate of lithium, owing to the presence of sulphate of ammonium.

Having mentioned these facts, I must describe the preparation of carbonate of lithium, which was done on two different occasions by M. Rommelaere, working each time on 500 grms. of commercial carbonate of lithium.

I will first describe the method as it was originally followed, and I will then point out the modifications I thought necessary to introduce into it.

The carbonate, suspended in five times its weight of water, was dissolved in nitric acid in such a way as to obtain a solution of nitrate and carbonate of lithium. The solution, contained in a large flask with a ground-glass stopper, was saturated with sulphuric acid, and left in it for twenty-four hours. After it had become clear and colourless, it was filtered and collected in another large flask, and the clear liquid was kept boiling for some time, to eliminate the carbonates of lithium and magnesium. The nitrate solution, having settled and having been filtered, received successively an excess of pure oxalate of ammonium to precipitate the calcium, and, having settled and having been re-filtered, an excess of baryta water to eliminate the final traces of magnesium; finally, after having settled and been filtered once more, an excess of sulphate of ammonium, to precipitate the barium.

As the liquid holding the sulphate of barium in suspension did not pass clear through a double filter-paper, notwithstanding it had been boiled, it was left to settle naturally, which took a very long time. Having become clear, it was decanted, filtered, and evaporated to dryness in a porcelain dish; the nitrate was melted and poured into a platinum dish. The colourless mass with an alkaline reaction was immediately powdered, put into a flask with a ground-glass stopper, and taken up by the least possible quantity of absolute alcohol necessary to dissolve the nitrate of lithium. To this solution was added some anhydrous ether until a small part of the lithium salt was precipitated; it was then left to settle naturally. This having happened, the flask was put in a freezing mixture of sea-salt and ice. The liquid in it was slightly clouded, and the flask was kept at a low temperature until the liquid was quite clear; it was carefully decanted, fil-

tered, and evaporated to dryness in a glass flask. The nitrate was taken up by the least possible amount of water, and the solution was precipitated by an excess of concentrated ammonia, saturated with sesquicarbonate of ammonium.

The flask was heated on a water-bath until ammonia gas was freely given off. When the carbonate of lithium, from being gelatinous, had become granular, it was poured into a funnel furnished with a clean linen plug. The elimination of the filtrate, and washing with water containing bicarbonate of ammonium, and then with pure water, were done with the filter-pump.

The carbonate of lithium was taken up by nitric acid; and the nitrate solution, which was quite *clear*, was precipitated a second time by sesqui-carbonate of ammonium. The separation of the filtrate and washing with carbonate of lithium were effected as described above. Lastly, all these operations were repeated a third time.

This carbonate of lithium, in a Bunsen flame, showed a comparatively strong sodium spectrum as well as the red lithium line, *but no other line*.

As a check, I volatilised an appreciable quantity of the same carbonate in an *oxyhydrogen* blowpipe, on a platinum sheet.

When the *greater part* of the lithium was evaporated, and the temperature was raised to the fusing-point of platinum, the red and green lines of the calcium and barium spectra were visible, in addition to the three lithium lines.

This experiment was tried several times, and always with the same result. There is no doubt the solution of nitrate of lithium in *etherised absolute alcohol*, made as I have just described, contained, besides sodium, barium and calcium.

It was heated, so as to completely volatilise the oxides of lithium, barium, and calcium, and there remained a *very slight* residue of silicate of barium and calcium, fusible but refractory, covering the platinum surface—which had been tarnished by oxide of lithium—with a thin white glaze.

A fresh preparation, most carefully made by M. Rommelaere in the same manner, gave exactly the same results.

The method I discovered, twenty-five years ago, of procuring carbonate of lithium, only purified it by reason of the successive re-solutions I made, in water saturated with carbonic acid, to get rid of the sodium. The barium and calcium were left in the undissolved portion of the carbonate of lithium.

The necessity for eliminating the barium and calcium as well as the silica, and avoiding the attack on glass vessels by sesqui-carbonate of ammonium, which introduced silicon, calcium, and sodium, led me to submit the carbonate of lithium, purified as I have just described, to the following treatment:—The salt was dissolved in sulphuric acid that had been distilled in a platinum vessel and diluted with water. The solution was evaporated to dryness in a platinum retort, and the sulphate heated to drive off the excess of sulphuric acid and render the silica insoluble. The sulphate of lithium when cold was translucent, showing white specks. When taken up by water, it made a slightly clouded solution, which was left in the platinum dish to settle. As an extra precaution, it was filtered through a double paper, which had been previously treated with dilute hydrofluoric and hydrochloric acids, then washed with pure water, and collected in a large platinum dish, where an 80 per cent solution of alcohol was added until a noticeable quantity of sulphate of lithium was precipitated, because of its slight solubility in alcohol.* The supernatant liquid was left under a bell-jar, to settle; this took a long time: then it was filtered again, and finally heated in a platinum retort to drive off the alcohol. I then precipitated the sulphate of lithium

* I ascertained these facts by dissolving 0.1 grm. of pure iron in aqua regia, and then turning the solution into almost boiling ammoniated water in a beaker. The above-mentioned ferric hydrate was collected in a filter which had been washed with a mixture of dilute hydrofluoric and hydrochloric acids, and then with water. The filter, when dried, was burnt, and the ferric oxide was put into a platinum boat contained in a carbon boat, which was brought to a dull red heat in a porcelain tube, in a slow current of hydrochloric acid gas. The volatilised ferric oxide left 0.011 grm. of perfectly white silica, containing traces of lime, but quite soluble in dilute hydrofluoric and hydrochloric acids.

* I satisfied myself that the sulphate of lithium above mentioned was mixed with a *very small* amount of barium and calcium.

in the same platinum dish, by carbonate of ammonium prepared in another platinum dish, using for this purpose a rubber tube to introduce the ammonia and the carbonic acid gas into the water. After having heated the gelatinous precipitated carbonate of lithium for a long time, in order to make it granular (a state in which part of the decomposed sulphate re-combines, but which is necessary in order to be able to wash the precipitate), the filtrate was decanted, as much as possible was drawn off by suction, and, following the example of Berzelius, the sulphate and the sesqui-carbonate of ammonium were separated, by washing the precipitate with alcohol so diluted as not to cloud the filtrate. Berzelius recommended 99 per cent alcohol to wash a carbonate precipitated from a chloride; he had to use 60 per cent alcohol, which sensibly dissolved the carbonate, so as not to make the double sulphate of lithium and ammonium adhering to the precipitate insoluble; after washing in dilute alcohol had removed all the sesqui-carbonate of ammonium, the precipitate was poured into a funnel with a clean linen plug, connected with a filter-pump, and the washing with dilute alcohol was continued so long as the liquid clouded an acid solution of acetate of barium: this took a long time, and necessitated dissolving a noticeable amount of carbonate of lithium. When this result was reached, I put part of the precipitate into a hydrogen flame; the sodium line showed very faintly. I did not see either the red or orange lithium lines. I then heated part of the same carbonate on a platinum sheet in an oxyhydrogen blowpipe; it was *completely* volatilised. No trace of the calcium spectrum appeared; there was a faint suspicion of the presence of a very weak image of the barium spectrum.

The carbonate of lithium, which weighed more than 200 grms., was divided into two parts, A and B.

The part A was dissolved in dilute pure sulphuric acid; the solution was evaporated to dryness in a platinum retort, and the sulphate was melted. The salt was treated as I have described for the sulphate first made, and the resulting carbonate, after being properly washed in dilute alcohol, was *entirely* volatilised in an oxyhydrogen blowpipe, without which it would not have been possible to detect, by spectrum analysis, the most transient appearance of the calcium or barium spectrum. *Part of this carbonate was used to identify the luminous spectrum of oxide of lithium.*

The part B of the carbonate of lithium was heated almost to fusion in a covered platinum crucible. This salt was then suspended in water contained in a platinum retort, and subjected to a current of pure carbonic acid. When a small portion of the carbonate was dissolved, the current was stopped, and the liquid left undisturbed. After it had settled, the clear liquid was decanted, and the carbonate was submitted to a fresh wash in dilute alcohol. The washings were put back into the decanted carbonate solution, and the whole was evaporated at boiling-point in a platinum vessel down to three-quarters of its volume.

The deposited carbonate of lithium was turned out; the filtrate, when concentrated in a small platinum dish, showed a very strong sodic reaction, but showed no reaction with an acid solution of acetate of barium. A certain quantity of sulphate of sodium or lithium, capable of being removed by a barium salt, had been eliminated.

Having found these facts, part of the lithium left in the retort was dissolved. For this purpose a current of carbonic acid was passed into the water containing the salt in suspension, until it was saturated; *nine-tenths* of the carbonate in the retort was then gradually dissolved. The liquid, having become clear by standing, was boiled in a covered platinum dish, to drive off the carbonic acid and cause the deposit of the carbonate held in solution. I found thus that a litre of saturated liquid deposited from 38 to 39 grms. of carbonate of lithium. Care was taken to entirely change the filtrate, which was again saturated with lithium salts.

Having washed the deposited carbonate of lithium,

several times, with pure alcohol, it was dried and redissolved in water saturated with carbonic acid, always working with platinum dishes.

The salt which was deposited by boiling the solution, and washed again with pure alcohol, was used to check the results given by the carbonate made from sulphate, but which had not been dissolved in carbonic acid.

The results were identical as regards the lithium spectrum; the only difference noticed was that, in order to get rid of the sodium D line in the oxyhydrogen blowpipe, it was necessary to volatilise about one-half of the carbonate precipitated direct from the sulphate, whilst the same result could be obtained by volatilising one-third of that which had been treated with carbonic acid as described.

I converted part of the carbonate, which had been twice dissolved in the anhydride, into sulphate, by means of sulphuric acid distilled in a platinum vessel; *from which carbonate I had eliminated the sodium by means of an oxyhydrogen blowpipe*, changing it into an oxide. This was the sulphate I used, side by side with part of the same salt made by M. Bunsen, to study the spectrum of this salt, which was found to be identical with that of oxide of lithium.

I tried to prepare some chloride from the oxide of the same carbonate of lithium, by working with hydrochloric acid gas in platinum vessels. Although I took all the care required for eliminating sodium from oxide of lithium, the chloride made showed the sodium line *until it was entirely volatilised*, both in a Bunsen burner and in an oxyhydrogen blowpipe. I doubt whether it be possible to obtain this body, or any substance as hygroscopic as it is, so pure as not to show the sodium line on spectrum analysis. I shall support this statement by plenty of evidence, when describing the results of my researches on the compounds of calcium.

It was this impossibility of preparing a chloride of lithium which would not show the sodium line which decided me not to use this compound to compare with the spectrum of lithium.*

(To be continued.)

THE DETERMINATION OF GRAPHITE IN PIG-IRON.

By P. W. SHIMER.

THE purpose of this note is to call attention to a source of error in the determination of graphitic carbon, made by the usual method of solution in hydrochloric acid. Although the method is tedious, because of the necessary treatment of the separated carbon with caustic potash, alcohol, and ether, the text-books seem to give it preference; and it is, perhaps, used more generally than the method of solution in dilute nitric acid. Solution in hydrochloric acid usually gives higher graphitic carbon results than solution in nitric acid, and many, therefore, consider it more trustworthy, the inference being that the lower results obtained by nitric acid are due to the loss of some of the finely-divided graphite by reason of the oxidising action of the solvent. But experiments made in Dr. Drown's laboratory, about seventeen years ago, showed no appreciable oxidation of graphite in the fifteen or twenty minutes' boiling required for the solution of a sample of pig-iron.

The point I desire to bring out here is, that the high results in graphitic carbon obtained by solution in hydro-

* All the chemical researches on the carbonates, sulphates, and chlorides of lithium described above were carried on in the chemical laboratory of the "Musée de l'Industrie," at Brussels. During the removal of this laboratory to the "Palais du Midi," the collection of lithium compounds, weighing more than 2½ kilogrms., was carried thither. When the laboratory of this "Palais" was burnt, the whole collection perished.

chloric acid are due to the presence in the graphitic residue of titanium carbide (see *Trans. Am. Inst. Min. Eng.*, xv., 455), and possibly of other insoluble carbides, the carbon of which is, of course, included with the graphite in the final determination. In the nitric acid method the titanium carbide is easily dissolved, and its carbon appears with the combined carbon, when the latter is determined by difference between graphitic and total carbon.

The method by solution in dilute sulphuric acid is open to the same objection as that by solution in hydrochloric acid; for titanium carbide is insoluble in sulphuric acid, and, I may add, it is also unattacked by hydrofluoric acid and by a boiling solution of caustic potash.

The following is an analysis of a pig-iron unusually high in titanium:—

	Per cent.
Silicon	3.650
Phosphorus	1.145
Sulphur	0.010
Manganese	0.226
Graphitic carbon	3.206
Combined carbon	0.128
Titanium	0.399
Iron (by difference)	91.236

100.000

The total carbon in this iron was determined by dissolving in an acidified solution of double chloride of copper and potassium, and subsequent combustion. The graphite was determined by solution in dilute nitric acid and combustion. A determination of graphite, made by solution in hydrochloric acid and combustion, gave 3.327 per cent of graphite, a result 0.121 per cent higher than that obtained by the nitric acid method. The amount of carbon combined as titanium carbide (TiC) with 0.399 per cent of titanium is 0.1 per cent, which counts as graphite in the determination by solution in hydrochloric acid. The results may be set down as follows:—

	Per cent.
Total carbon	3.334
Graphite by nitric acid solution	3.206
Graphite by hydrochloric acid solution	3.327

The error in the hydrochloric acid method falls heavily upon the resultant estimate of combined carbon, which is determined by difference, as appears below:—

	Per cent.
Combined carbon, when graphite is determined by nitric acid	0.128
Combined carbon, when graphite is determined by hydrochloric acid	0.007

An experiment was made to determine the action of boiling nitric acid (1.20 sp. gr.) on the graphite from this iron. A sample of 2 grms. was dissolved in hydrochloric acid (1.10 sp. gr.). After washing the graphitic residue with water, it was boiled gently for one hour with nitric acid (1.20 sp. gr.), with the addition of a little water from time to time, to keep up the bulk of the solution. The graphite, as thus determined, was 3.203 per cent against 3.206 per cent by direct solution in nitric acid, showing that the treatment for one hour, with boiling nitric acid, had dissolved out the titanium carbide without having attacked the graphite. The graphite in this high silicon iron, however, was coarse, and perhaps unusually resistant to the oxidising action of nitric acid. It is proposed to make similar experiments on the graphite from a variety of pig-irons.

The 0.128 per cent of combined carbon is made up as follows:—

	Per cent.
Carbon combined with 0.399 per cent titanium as TiC	0.100
Combined carbon soluble in hydrochloric acid (probably combined with iron and manganese)	0.007
Carbon possibly existing as insoluble carbide other than titanium carbide	0.021

A careful mechanical separation of a few grms. of titanium carbide was made from several pounds of this iron by use of the long, slightly inclined glass plane described in the paper before the Institute referred to above.

Besides titanium and carbon in this separation, there is some vanadium, apparently also existing as an insoluble carbide, which would account for a part of the above 0.021 per cent of combined carbon. This investigation is, however, still under way.

The writer has never encountered a pig-iron free from titanium, the amount found varying usually from 0.05 to 0.40 per cent. In irons with a coarsely crystalline fracture the cubical crystals of titanium carbide may always be found when carefully looked for. The conclusion seems to be fair that the hydrochloric acid method includes, with the graphite determined by it, the carbon existing as insoluble titanium carbide. With pig-irons containing from 0.05 to 0.40 per cent of titanium, the graphite so determined will be from 0.013 to 0.100 per cent too high, while the combined carbon will be correspondingly low.

It follows that more light would be thrown upon the condition of the carbon in pig-iron by making three determinations—viz., one of total carbon, one of the carbon insoluble in hydrochloric acid, and one of graphite by the nitric acid method. We would thus have determinations of graphitic carbon; carbon combined with iron and manganese, soluble in hydrochloric acid; and carbon combined as carbides insoluble in hydrochloric acid. In high-silicon, low-sulphur titaniferous irons, the insoluble form of combined carbon exceeds the carbon existing as soluble carbides of iron and manganese. It is important to know how the carbon is combined. One-tenth per cent of carbon combined with titanium in the condition of disseminated microscopic crystals, probably has no effect on the hardness of pig-iron; while the same amount of carbon, combined with iron and manganese, would have an appreciable hardening effect. Practically, therefore, it may be desirable to have the carbon existing as carbides insoluble in hydrochloric acid appear with the graphite as determined by the hydrochloric acid method, although the actual graphite can be determined only by solution in nitric acid. At all events it is essential to know by what method graphite has been determined, in order to draw conclusions from determinations of graphitic and combined carbon in pig-iron.—*Journ. Amer. Chem. Soc.*, vol. xvii., p. 873.

ON THE OXIDATION OF SOME GASES WITH PALLADINISED COPPER OXIDE.*

By E. D. CAMPBELL.

IN the work heretofore done on the combustion of gases where the well-known influence of finely divided palladium upon the ignition of gases has been taken advantage of, the oxygen for the combustion of the gas under examination has been introduced either as pure oxygen or diluted with nitrogen in the form of air. It was thought not impossible if palladium in sufficiently fine form and evenly distributed could be introduced into a solid reagent capable of giving up oxygen to combustible gases, that the temperature at which gases containing hydrogen would burn, might be lowered below the combustion-point in the absence of palladium, and that the differences in the temperatures of combustion of various gases might lead to a system of fractional combustion.

Copper oxide, being one of the most common reagents for combustion, and having the great advantage over most others of being easily re-oxidised after reduction, was thought to be the most desirable substance to work upon.

* Contributions from the Laboratory of Analytical Chemistry of the University of Michigan. From the *American Chemical Journal*, vol. xvii., No. 9, November, 1895.

Copper oxide, containing palladium very finely divided and evenly distributed throughout, was prepared in three ways; of these the first by which the oxide used in the combustion shown in the table was made, was as follows:—

An alloy was prepared by melting 600 grms. of fine copper and then adding 6 grms. of palladium. After melting this alloy was cast into a cold iron mould, then broken up and re-melted at a temperature nearly approaching the melting-point of palladium (considerably above that of copper), then quickly re-cast into cold iron moulds, the strips so cast being about 12 m.m. wide and 5 m.m. thick. Palladium did not seem to alloy very readily with copper, so that it was necessary to re-melt at a high heat and cool quickly to prevent the palladium from distributing itself in the form of a fine network, which rendered the alloy brittle when attempts were made to roll it. By re-melting at a high heat and quickly cooling an alloy was produced in which the palladium was evenly distributed, and which rolled as easily as pure copper. The strips of alloy thus produced were annealed like pure copper, then rolled until the thickness was reduced to 0.3 m.m., the width remaining about the same. These strips were then cut transversely into pieces 1.5 m.m. wide, thus giving small pieces 12 m.m. long, 1.5 m.m. wide, and 0.3 m.m. thick. About 160 grms. of this alloy was introduced into a combustion-tube of 16 m.m. internal diameter, the alloy being retained in position at both ends by plugs of copper gauze. The column of alloy was 34 c.m. long. The combustion-tube so prepared was placed in an ordinary Bunsen combustion-furnace, brought to a moderate red heat, and purified oxygen passed through as long as it was taken up.

Second Method.—In the course of the work, owing to frequent reduction and re-oxidation of the copper, and to handling of the oxide in filling or emptying tubes, a considerable amount of fine oxide accumulated which could not be used as it was without choking the tube. This fine oxide was ground until it would pass through a 100-mesh sieve, mixed with thick mucilage to a rather stiff paste, and pressed by means of a sodium press into wire a little less than 2 m.m. in diameter. This wire, after it had become dry, was broken into pieces about 10–12 m.m. long, introduced into a platinum crucible, and heated to a moderate red heat until all volatile matter ceased coming off. The wire so produced was strong enough to retain its form perfectly while introducing it into a combustion-tube in which it could be completely oxidised by means of oxygen at a red heat.

Third Method.—This method was not worked out until the combustions shown in the table were completed, but it is recommended as the best method for the purpose of preparing the oxide, as it is much simpler than either of the previous methods, and the oxide prepared by it we have shown by quantitative combustion of hydrogen is fully as efficient as that produced by the first or second method. The method is as follows:—3 grms. of palladium wire was dissolved in a moderately-sized casserole by means of 40 c.c. of nitric acid (sp. gr. 1.42), to which was added 10 c.c. of hydrochloric acid (sp. gr. 1.20). After evaporating to dryness on the water bath the palladium was brought into solution with 10 c.c. of nitric acid, 3 c.c. of hydrochloric acid, and sufficient water to bring the volume to 60 c.c. Into this solution was introduced 300 grms. of pure copper oxide, previously ground to pass through a 100-mesh sieve. This produced a very stiff paste, which after thorough mixing was dried at 120° and again ground to pass through a 100-mesh sieve. The fine ground oxide so produced was then mixed with mucilage, pressed into wire, dried and ignited like that in the second method of preparation.

In order to control the temperature of the tube at any time a special form of air jacket was made, in two halves, so that it could be put on when the combustion-tube was used for combustion, or removed when it was desired to re-oxidise the copper without disturbing the position of

the tube. The jacket consisted of two halves of a heavy brass tube 3 m.m. thick, 52 m.m. internal diameter, and 48 c.m. long; this internal diameter allowed the jacket to surround the combustion-tube and its gutter and still leave a clear space of 5 to 7 m.m., thus heating the tube entirely by radiation. The thickness of the inner brass tube also tended to equalise the temperature and to prevent sudden variations. The two halves of this inner brass tube were joined at both ends to an outer heavy sheet-iron tube, leaving between the tubes an annular space of 7 m.m. The two halves of outer sheet-iron tube came together on the under side in the form of a lap joint, and were prolonged on the upper side so as to be supported by means of metal pins on both sides of the double horizontal bar at the top of the furnace usually used to keep the tiles apart. Through the double bar at the top of the furnace, and through three holes in the inner brass tube, were introduced three nitrogen-filled thermometers capable of registering 460°. These thermometers reached to and rested on the inner combustion-tube. In addition to this jacket on each side of the furnace were provided two sheet-iron guards to prevent currents of air and to maintain a steadier heat. In addition to these a heavy sheet-iron gutter, 54 m.m. wide and 48 c.m. long, was curved to fit the under side of the outer jacket, and when wired to it could take the direct heat of the flame and prevent the burning out of the outer jacket. This gutter was found necessary when working at the higher heats. Thus provided, the inner combustion tube was so placed that it was heated by radiation from the heavy inner brass tube, which was in turn heated by radiation from the outer sheet-iron jacket. In this way a steady even temperature of the combustion-tube could be maintained at any temperature up to 450°, and the entire jacket could be easily removed, the tiles put back in their usual place, and the copper re-oxidised without disturbing the combustion-tube.

In determining the initial combustion-point of any gas, a moderate flow of the pure gas was kept passing through the combustion tube, to the farther end of which was attached a small tube containing glass-wool sprinkled with anhydrous cupric sulphate, for the detection of moisture, followed by a U tube containing a clear solution of calcium hydrate for the detection of carbon dioxide. The temperature of the tube was gradually raised, the three thermometers being kept within a range of 5° until a test for moisture and carbon dioxide was obtained. As soon as this was done in any case the supply of gas was shut off and pure dry air drawn through the tube, the temperature allowed to fall below the ignition-point, the gas turned on again, and the temperature again carefully brought up until a second test was obtained. In gases containing both carbon and hydrogen, a test for carbon dioxide was obtained always a little in advance of that for moisture. This difference is probably accounted for by the greater sensitiveness of calcium hydrate for carbon dioxide than that of hydrous cupric sulphate for moisture. In the table of results the limits of temperature given include those at which distinct test for both moisture and carbon dioxide were obtained. In determining the ignition-point of a gas it was also found necessary to use the combustion-tube after it had been used for a quantitative combustion, since a freshly re-oxidised tube was found to contain small amounts of palladious oxide, which gives up its oxygen very much more readily than the copper oxide, and which would consequently make the ignition-point apparently much lower than its true value.

For the quantitative combustion of gases, the inlet end of the combustion-tube was connected to a T tube provided with a three-way stop-cock, by means of which either the pure dry gas under examination could be introduced into the tube, or by reversing the cock pure dry air or oxygen could be drawn or forced through the tube for the purpose of sweeping forward the products of combustion or for re-oxidising the copper when desired.

(To be continued).

NOTICES OF BOOKS.

The Factory Acts. By the late ALEXANDER REDGRAVE, C.B., Her Majesty's Chief Inspector of Factories, &c. Sixth Edition. Including the Act of 1895. By JESSE A. REDGRAVE, One of Her Majesty's Inspectors of Factories; and H. S. SCRIVENER, M.A. Oxon, of the Middle Temple, Barrister-at-Law. London: Shaw and Sons, and Butterworth and Co. 1895. Pp. 356.

THE legislation concerning factories and workshops is not only voluminous in itself, but has been complicated by the partial repeal of certain Acts. Hence the work before us is useful not merely to manufacturers who wish to know when they are obeying the law, but also to solicitors and to the inspectors themselves. No fewer than nine Acts of Parliament are here quoted in full; nine others are given in part.

It is satisfactory to find that the expressions "factory" and "workshop" are now officially defined. It is also satisfactory that certain judicial decisions are given touching questions which might furnish scope for quibbling. The phrase "a Secretary of State," or, at greater length, "one of Her Majesty's principal Secretaries of State," might be judiciously altered. The "Home Secretary" would in every case be a happier expression, except where the manufactory of explosives, &c., for the War Department is concerned. We notice that print-works, bleach- and dye-works, chemical- and colour-works are admitted to be non-textile factories, and are consequently exempted from certain regulations which would then be useless and annoying.

It appears that a special notice of any case of lead-, phosphorus- or arsenic-poisoning, or anthrax, is a new and justifiable provision. But we are informed, in a note, that the Secretary of State may apply it by order to any disease occurring in a factory or workshop. Now, it would not be difficult to name diseases the occurrence of which has no connection with the sanitary conditions of a factory or with the processes there carried on.

A provision given on p. 236 will, we may hope, touch manufacturers of clothing who give out materials to be made up in unsanitary localities.

In fine, the Acts and provisions here quoted or abstracted seem to be just and needful, and the work before us may hence be regarded as valuable and deserving recommendation.

Practical Inorganic Chemistry. By G. S. TURPIN, M.A., D.Sc., Head Master of the Intermediate and Technical School, Swansea. London and New York: Macmillan and Co. 1895. Pp. 158.

IT is to be hoped that some time the abundant treatises on the various sciences, and especially on chemistry, will begin to germinate and yield a harvest. As a rule, like the little volume before us, they contain nothing erroneous in fact or mistaken in generalisation. But for all this we are left in painful doubt as to their *raison d'être*, and we are driven to hope that the issue of elementary treatises might be suspended pending the avatar of some capital discovery, such, *e.g.*, as the decomposition or the synthesis of some one of the elements.

Helps to Health and Beauty. Two Hundred Practical Prescriptions. By A PHARMACEUTICAL CHEMIST. London: James Clarke and Co. (Fleet Street). 1895. Pp. 117.

THIS little work is of a character rarely noticed in our pages. The substances here mentioned, whether medicines or cosmetics, are, with rare exceptions, not combinations, but mixtures. The author, however, is decidedly master of his subject. We must note, as an instance in proof, that he insists on the superiority of English oil of

lavender—the growth of Mitcham or Sandy—to that of foreign growth for the manufacture of perfumes. The recommendation of the florets of *Pyrethrum roseum* as an insecticide is strongly to be approved of. It is strange that, whilst in the colonies of Australia and South Africa country fit for the cultivation of the plant exists in square miles, the inhabitants still submit to be bitten, stung, and buzzed about by noxious insects.

It might have not been amiss if the author had called attention to the value of marsh rosemary (*Sedum palustre*) as a preservative against mosquitoes and sand-flies.

The Physiology of the Carbohydrates: an Epi-criticism. By F. W. PAVY, M.D., LL.D., F.R.S., Fellow of the Royal College of Physicians, &c. London: J. and A. Churchill. 1895. Pp. 141.

THIS book is concerned with a controversy concerning the "glycogenic theory." Does the liver, as Dr. Noel Paton contends, generate sugar? or is this viscus, as Dr. Pavy shows, a sugar destroyer? The question is complicated by the fact that Dr. Paton's support of the glycogenic theory has found its way into the *Philosophical Transactions of the Royal Society*, in a memoir not quite free from personalities. The President and Council have certainly, in a private letter to Dr. Pavy, expressed their regret that this paper should ever have been suffered to appear; but this does not undo the fact and the effects of its publication. Dr. Pavy, as regards the "glycogenic theory," appears to be in the right.

Molecules and the Molecular Theory of Matter. By A. D. RESTEEN, S.B. Boston (U.S.A.) and London: Ginn and Co. 1895. 8vo., pp. 223.

THE author of this ably-written work opens his Preface with the remark that "In the multiplication of popular books on scientific subjects the molecular theory of matter seems to have been strangely neglected." Hence we may fairly infer that Mr. Resteen intended to produce a treatise which should be intelligible to the cultivated public, and at least to men of Science whose speciality is not mathematical. How such works might be written on physical subjects it may be seen from the examples set by Tyndall. Our author, however, if such was his intention, has failed in its execution. His work, however valuable, will not be as a whole available to any one who has not a full command of the resources of the higher mathematics. It must further be kept in mind that he treats of molecules in their physical aspect, referring the reader for the chemical phase of the subject to the writings of Meyer, Remsen, Ostwald, and Mendeleeff.

After a section on general considerations, in which a distinction is drawn between molecules and atoms, we proceed to the kinetic theory of gases. Here we have an exposition of the law of Avogadro and Boyle, and a survey of the phenomena of high vacua, with an appreciative notice of the researches of Mr. Crookes, F.R.S., in this direction.

The molecular theories of liquids and solids form the subject of two succeeding sections. In the remaining sections we have a discussion of molecular magnitudes and of the constitution of molecules. The conclusion reached is, that "something is known of the constitution of gases, a little of the constitution of liquids, and almost nothing, for certain, of solids." About the constitution of molecules, and the mechanical nature of intermolecular forces, nothing whatever is yet known.

The hypothesis of Prout is, as we need scarcely say, rejected. On the ultimate unity of matter Mr. Resteen does not pronounce decidedly; nor does he speculate on the possible origin of the elements. Yet that he is not devoid of the scientific imagination we may gather from his speculations on the conservation of weight. He does not see any warrant for the ordinary assumption "that when an atom whose weight is A combines with another

atom whose weight is B the weight of the resulting molecule is universally and necessarily $A+B$." He does not ignore the consequences which must follow from his suggestion, if it should ever be verified; nor does he adduce any phenomena in its support. He thinks that his hypothesis explains both the existence of elements and the slight deviation from integral values which we find in their atomic weights. Mr. Resteen ascribes the entire merit of the discovery of the "Periodic Law" to Meyer and Mendeleeff, and rejects the analogy suggested between the periodic law of the elements and the astronomical law of Bode.

Could the work before us be divested of its mathematical scaffolding it would merit, and doubtless receive, a very general appreciation.

CORRESPONDENCE.

ON THE PLACE OF HELIUM IN THE CLASSIFICATION OF ELEMENTARY SUBSTANCES.

To the Editor of the Chemical News.

SIR,—Mr. Gladstone complains of the tone of my criticism which has been adopted to meet his peculiar controversial methods in dealing with questions of vital importance to the future progress of chemical science. As he appeals to chemists who are interested in the questions of priority, raised incidentally in this discussion, to judge for themselves, it will facilitate the enquiry if I point out that Dr. Gladstone, in the reference to his paper in the *Philosophical Magazine*, May, 1853, has put forward the old atomic weights, 16 and 24, as anticipating the same numbers in my table, which, as every chemist knows, are double the old atomic values.

The vertical series of constant differences, 16, 16, 24, 24, 24, advanced by Dr. Gladstone as new in the year 1883, are the same as those in the series H_{2n} of my table of 1878, as shown in my letter to the *CHEMICAL NEWS* of December 13th last. As there is an absolute parallelism between the constant differences of the atomic weights of the first and second series, H_n , H_{2n} , Dr. Gladstone has himself furnished full proof that the differences of the atomic weights of the first group or series in Mendeleeff's table and in my own do not increase as we go downwards as he alleged.

Now that the question of the place of helium in the classification of the elements is definitely raised in the *CHEMICAL NEWS*, I will, with your permission, make a few remarks on the periodicity of chemical properties which is supposed to exist when the elements are arranged in seriatim order of their atomic weights. In a paper which I read before the Manchester Literary and Philosophical Society on December 11th, 1894, it was proved that, when such an arrangement of the atomic weights was rightly adhered to, the idea of recurring properties or periodic functions has no real foundation in nature. It was also demonstrated by means of two tables, A and B, that, when a new element x was brought into the series, the order of the whole system vanished, and that the predictions of the properties of unknown elements, so far from being the result of the so-called periodic law, were made in spite of it.

In the *CHEMICAL NEWS* of December 20th last another attempt is made, by Mr. R. M. Deeley, to bring helium into a periodic system. Tables I. and II. in his communication demonstrated the fallacies involved in the periodic system so much more forcibly than the demonstration given in my paper, that a first examination of these tables left the impression that Mr. Deeley was a humorist adopting an ironical method of bringing the periodic system into ridicule. His papers in the *Trans-*

actions of the Chemical Society, to which he refers, and his last communication to the *CHEMICAL NEWS* show, however, that Mr. Deeley is an earnest student, endeavouring to reconcile the facts of his science with the impossibilities involved in a classification based on an imaginary periodicity of chemical properties when the elements are arranged in the proper order of their atomic weights. Mr. Deeley's papers and tables deserve the serious attention of all who are interested in the progress of chemical philosophy.—I am, &c.,

HENRY WILDE.

January 14th, 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 25, December 16, 1895.

Composition of the Flours furnished by Grinding Soft Wheats and Hard Wheats in Cylinders.—Aimé Girard.—From the analytical and practical study of the produce of three grindings executed under the superintendence of the Commission, it appears distinctly that the limit of the yield in flour fit for the manufacture of white bread, porous, well-risen, and easily digestible, as modern consumption requires, lies between 60 and 65 per cent of the weight of the wheat. Beyond this point, we find about 5 per cent of mealy product, decidedly acid, and calculated to yield only compact loaves, flat, with a greasy crumb, dark coloured, loaded with water, and difficult of digestion.

Direct Combination of Atmospheric Nitrogen with the Metals in the form of Magnesium, Aluminium, Iron, Copper, &c., Nitrides.—A. Rossel.—The author, in conjunction with Léon Frank, has established that it is not the same if we heat pulverised calcium carbide with magnesium in powder to dull redness either in a porcelain crucible or in a tube in which the atmospheric air circulates freely. The reaction takes place in a regular manner—layers of pulverised calcium carbide and of magnesium in fine powder. The product, freed mechanically from the lime, leads on analysis to the formula Mg_3N_2 . The residue in the crucible contains as much as 23.8 per cent of nitrogen, obtained from the atmospheric air. Aluminium, zinc, iron, and even copper, if treated in the same manner, give similar reactions, forming products decomposable by water, and more readily by dilute potassa lye. These reactions are an additional proof, as Moissan has pointed out, that at the epoch of the formation of the earliest geological strata nitrogen did not exist in the free state, but in combination with metals.

Preparation and the Properties of Crystalline Chromium Sulphide.—A. Mourlot.—The author shows that the sulphide formed by the action of hydrogen sulphide upon metallic chromium is a protosulphide. By an increase of temperature, he has effected the crystallisation of this substance. The sulphide has a great stability.

Lithium Subchloride.—M. Guntz.—On heating in a nickel crucible, and in a current of hydrogen, 27.4 grms. $LiCl$ and 4.7 grms. metallic lithium to dull redness, we obtain a melted product, slightly greyish, very hard, and homogeneous. It has the composition Li_2Cl , and decomposes water as readily as does lithium itself. The metal absorbs nitrogen very readily.

Certain Novel Safranines.—G. F. Jaubert.—The author has undertaken to produce the simplest possible safranines containing an alcoholic radicle linked to azinic nitrogen.

He has formed a methylic derivative, metho-safranin; an ethylic compound; etho-safranin, and two naphthyl derivatives, α and β naphtho-safranines.

Study of *Aspergillus Orizæ*.—E. Sorel.—The author has verified the accuracy of the observation of Jubler and Joergenson that *Aspergillus orizæ* is transformed into a *saccharomyces*.

Researches on the Influence of Electricity on the Development of the Embryo of the Fowl.—Camille Dareste.—The germ is not affected in its material constitution by electric influences which destroy adult animals of a certain bulk (?) But the germ is nevertheless modified, in a majority of cases presenting teratological phenomena.

Study of the Action of various Radiations of the Solar Spectrum upon Plants.—C. Flammariou.—The observations were made upon sensitive plants growing respectively in houses of red, green, and blue glass; a house of ordinary white glass serving as a check. The growth in height followed the order—red, green, white, blue. In vigour and activity of vegetation, the order was—red, white, green, blue. Under blue glass the vegetation was very feeble. The action of red light is compared to that of a chemical manure.

No. 26, December 23, 1895.

This issue gives the account of the usual Public Session of the Academy, with obituary notices of deceased Members and Associates. Pasteur received the well-merited eulogium, and there was also honourable mention of Verneuil, of Larrey, of Cayley, Dana, Vogt, Lovén, Hellriegel, and Huxley. The last-mentioned *savant* was especially characterised as a reformer of higher education, as one who had reproached the ancient universities of Oxford and Cambridge for having forsaken their true task, and from being nurseries of study and research, they have sunk down to be boarding-schools for wealthy youths. The speaker further denounced the small share of attention granted to Natural Science. The Grand Prize for the Physical Sciences has been awarded to Charles Brongniart for his paleontological researches on the coal-beds of Commeny. The Biennial Prize has been allotted to M. Raoult for researches on molecular precipitations, and their application to the sanitation of unwholesome industries. The Leconte Prize has been awarded to Lord Rayleigh and Professor Ramsay for their well-known researches on the constitution of atmospheric air. The prize offered by Alberto Levi for a remedy for diphtheria has been granted to Dr. Behring.

MEETINGS FOR THE WEEK.

- MONDAY, 20th.—Society of Arts, 8. (Cantor Lectures). "Alternate Current Transformers," by Dr. J. A. Fleming, F.R.S.
- TUESDAY, 21st.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.
- Institute of Civil Engineers, 8.
- Pathological, 8.30.
- Photographic, 8.
- WEDNESDAY, 22nd.—Society of Arts, 8. "Supply of Sea-Water to London," by Frank W. Grierson.
- Geological, 8.
- THURSDAY, 23rd.—Royal, 4.30.
- Chemical, 8. Helmholtz Memorial Lecture, by Prof. G. F. Fitzgerald, F.R.S.
- Institute of Electrical Engineers, 8.
- Royal Institution, 3. "Dante," by Philip H. Wicksteed, M.A.
- FRIDAY, 24th.—Royal Institution, 9. "Ludwig and Vitalism," by Prof. Burdon Sanderson, M.D., F.R.S.
- Physical, 5. Exhibition of some Geometrical Instruments, by E. Scott and Signor Monticolo. "On Resultant Tones," by J. D. Everett. Experiments with Incandescent Lamps, by Sir David Salomans.
- SATURDAY, 25th.—Royal Institution, 3. "The Valley of Kashmir," by Walter R. Lawrence, I.C.S.

KING'S COLLEGE, LONDON.

Laboratory Attendant required in the State Medicine Laboratory.—Apply to WALTER SMITH, Esq., Secretary, King's College, Strand, W.C.

Chemist and Assayer Wanted; well up in methods for estimation of Copper, Antimony, Lead, Gold, and Silver.—State age, qualifications, experience, references, and salary required, to A. B., The Sheffield Smelting Co., Ltd., Sheffield.

Wanted, a trained Chemist for the Dye-work of a firm dyeing first-class fancy cotton goods; must be capable of superintending dyeing operations and undertaking Analytical Work; a Fellow of the Institute preferred.—Apply, stating age, qualifications, references, and salary, to D. W., CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

Wanted, competent Man, with practical experience in Metallurgy of Silver, Lead, and Copper, dry and wet methods; to superintend Works operations and act as Assayer and Chemist.—Full particulars to "Provincial," CHEMICAL NEWS Office, Boy Court, Ludgate Hill, London, E.C.

Wanted, a Manager for Acid Industries in South Africa. Competent Man required for Administration. Thorough knowledge of Sulphuric Acid manufactory and branch industries indispensable. Experience in treatment of Gold Ore by chlorination preferred. Only first-class men need apply. Testimonials and references required. State salary.—Letters, G. S., care of A. Siegle, 30, Lime Street, London, E.C.

NOTICE TO ANALYSTS AND LABORATORY DIRECTORS.

Best METHYLATED SPIRIT, manufactured by A. & J. WARREN, Wholesale Druggists, Dealers in Chemicals for Analytical Work, and Methylated Spirit Makers, 23 and 24, Redcliffe Street, Bristol. For Four-pence a Pamphlet on Methylated Spirit, written by Algernon Warren, is obtainable from the Publisher J. W. ARROWSMITH, Quay Street, Bristol; and SIMPKIN, MARSHALL, HAMILTON, KENT, and Co., Ltd., London.

NOTICE.

JOHN CLIFF & SONS, EXCHANGE CHAMBERS, LEEDS, wish to SELL (preferred) or LET their Chemical Stoneware and Pipe Pottery, at Runcorn, upon Manchester Ship Canal (and scheduled for purchase), with view of OPENING AT LEEDS, near their headquarters.

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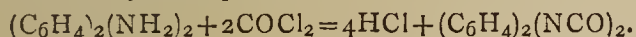
VOL. LXXIII., No. 1887.

THE ACTION OF DIPHENYLENE DI-ISOCYANATE UPON AMIDO-COMPOUNDS.

By H. LLOYD SNAPE, D.Sc., Ph.D.

THE preparation of diphenylene cyanate I described some years ago (*Journ. Chem. Soc.*, xlix., 255); and I then showed that, like phenyl iso-cyanate, it readily entered into combination with alcohol and phenol respectively, forming the corresponding carbamates. It seemed probable that the similarity would extend to the behaviour of the new cyanate towards ammonia and aniline; and this I have found to be the case.

The method by which I obtained the dicyanate consisted in heating the benzidine hydrochloride (the salt being preferable to the base, because it is more stable) successively in benzoic acid and diphenylamine vapours, in a current of phosgene gas, the ultimate reaction being represented by the equation—



In repeating this, to prepare a fresh quantity of the cyanate for my present experiments, I found that it was unnecessary to regulate so rigidly the temperature, and that even a better yield could be obtained on heating the benzidine salt in a rapid current of phosgene (generated by very gently heating its solution in toluene) by a smoky gas flame, allowing the temperature to gradually rise until the deposition of solid cyanate in the neck of the tubulated retort employed, ceased. The yield still leaves much to be desired, owing apparently to the intermediate formation of diphenylene urea, which is only partially attacked by the excess of phosgene.



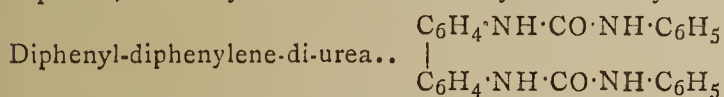
Ammonia gas was conducted into an ethereal solution of the diphenylene dicyanate, when a white crystalline compound at once separated. This was purified by solution in concentrated sulphuric acid and precipitation by water, and was submitted to analysis.

0.076 grm. yielded 13.6 c.c. N at 15° and 761 m.m.

Per cent N.

Found	20.98
Required for $C_{14}H_{14}N_4O_2$.. .	20.74

The substance possessed all the characteristics named by H. Schiff (*Berichte d. D. Chem. Gesell.*, xi., 833) of that obtained by him by heating benzidine with urea. He does not give the structural formula of the compound nor his analytical data, but merely states that the composition may be thus described, $C_{12}H_8(NH_2)_2 + 2CO(NH_2)_2 - 2NH_3$. This, however, is not discordant with the formula given above; and the substance prepared by him is, as I had expected, evidently identical with that synthesised by me.



Dilute ethereal solutions of diphenylene dicyanate and aniline were mixed together, and after an interval of one or two minutes, a white precipitate suddenly separated. This was soluble in hot aniline and, even at ordinary temperatures, in sulphuric acid. From the former solution it separated on cooling in small crystals, but from the latter solution it was precipitated, on the addition of

water, in amorphous gelatinous form. The compound proved to be, as I had anticipated, identical with that obtained by B. Kühn (*Berichte d. D. Chem. Gesell.*, xviii., 1478) from benzidine and phenyl isocyanate. Analysis gave the following result:—

0.106 grm. yielded 12.3 c.c. N at 15° and 754 m.m.

Per cent N.

Found	13.48
Calculated for $C_{26}H_{22}N_4O_2$.. .	13.27

Hence diphenylene dicyanate behaves like other isocyanates towards amido-compounds.

University College of Wales, Aberystwyth.

ELECTRO-DISSOLUTION AND ITS USES.

By H. N. WARREN, Research Analyst.

ON the same principle that electro-dissolution is used for the estimation of combined carbon in steel, &c., I have lately varied the experiment by introducing—instead of steel—iron containing a certain percentage of boron, and, having connected the respective boride with the positive pole of a powerful battery, and to the negative a plate of platinum, using as a solvent dilute sulphuric acid, I observed, after the lapse of about twelve hours, that the iron had entirely passed into solution, and a considerable amount of brownish precipitate had collected at the bottom of the vessel, intercepted by flakes of graphite and carbon. The precipitate, having been collected on a filter-paper, washed, and dried, proved on examination to be amorphous boron, containing graphite and other impurities, which had become chemically introduced during the preparation of the boron compound. The boron was next introduced into a small clay crucible, and intensely heated in a current of hydrogen gas, for the purpose of rendering it more dense and destroying its pyrophoric properties; and was, lastly, introduced into a combustion-tube and heated to redness in an atmosphere of carbonic anhydride, in order to separate the carbon; pure boron was finally obtained.

In like manner silicon-eisen, containing 9 per cent of silicon, was treated, but the result was not so satisfactory; only a small quantity of silicon separates in the uncombined form, the greater quantity separating in the form of silica, SiO_2 , the amorphous silicon being apparently more prone to oxidation than the boron so obtained.

Ferrous sulphide was next similarly treated, and gave, after the lapse of a few hours, a copious blackish precipitation of sulphur, and possessing properties similar to the sulphur obtained by dissolving sulphides, such as cupric sulphide in dilute nitric acid,—in all other respects resembling common sulphur. Phosphides of iron, zinc, &c., were next introduced, and gave, besides carbon and other impurities, a residue containing a large percentage of phosphorus, which differed from ordinary phosphorus with respect to its insolubility in carbon disulphide, and resembled the reaction afforded in the case of silicon-eisen, rather than that of the boron compound, inasmuch that a large quantity of phosphorus had passed into solution. A rod of impure copper—containing arsenic, iron, zinc, and other impurities—was next substituted, using hydrochloric acid as a solvent in place of sulphuric acid. In the course of a day the copper had entirely dissolved and precipitated itself in the negative electrode, the impurities remaining in solution.

The copper, after having been washed, dried, and weighed, gave identical results with regard to percentage with a careful gravimetric estimation.

I have lately used this method, and obtained excellent results with respect to the analysis of commercial copper, especially in the estimation of small quantities of arsenic, thus enabling the experimenter to form his investigation

on a much larger quantity than when precipitation is resorted to, at the same time avoiding the precipitated copper carrying down with it the arsenic. I have, in this manner, detected arsenic in commercial copper when all other methods have totally failed. Electro-dissolution may also be employed in the preparation of unstable compounds, such as stannic nitrate, potassic ferrate, ferric acetate, which are decomposed on the application of heat, and in some instances have succeeded by the means which follow of crystallising the resulting compound.

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CONTRIBUTIONS TO THE SEPARATION OF MERCURY FROM THE METALS OF THE ARSENIC AND COPPER GROUP.*

By CARL VON USLAR.

(Concluded from p. 29).

Separation of Mercury from Bismuth.

THE bismuth was always weighed as oxide. Before weighing it was again ignited and allowed to cool in the exsiccator. The separations, as in the case of the other metals, were effected both in a nitric and a hydrochloric solution. It was found, however, that a separation in a nitric solution gave values too low by from 1 to 2 per cent.

In order to prevent as far as possible a separation of basic bismuth chloride, a rather larger quantity of hydrochloric acid was employed, ranging from 20 to 30 c.c. The bismuth oxide, like the mercuric chloride, was first dissolved in the corresponding quantity of hydrochloric acid, then carefully diluted with hot water to 150 c.c.; the phosphorous acid was added to the cold liquid, and the whole digested in the manner already indicated.

The precipitate formed was filtered, washed with hot water containing hydrochloric acid (30 c.c. hydrochloric acid to 250 c.c. water) until no reaction of bismuth can be detected, and the liquid is once more mixed with phosphorous acid and digested. After prolonged standing there appeared a slight second precipitate.

The two precipitates were united, oxidised, and further treated as already described. On treatment with potassium-sulphide-potassium-hydroxide, there remained undissolved a slight brownish black precipitate of bismuth sulphide. It was afterwards united with the main quantity of the bismuth sulphide.

The filtrate containing the bismuth was first precipitated with hydrogen sulphide, and the precipitate of bismuth sulphide was tested for the presence of mercury sulphide by digestion with the mixture of potassium sulphide-potassium-hydroxide. Mercury was not detected in any of the precipitates.

The precipitates of bismuth sulphide were placed in a beaker and treated with hot concentrated nitric acid until the residues of the filters appeared of a pure white. The mixture was then diluted with hot water filtered off from the remnants of the filters, washed with hot dilute nitric acid until no blackening was produced on treatment with sulphuretted hydrogen water.

The filtrate was then evaporated down to a very small volume, slightly diluted with hot water after the expulsion of the nitric acid, neutralised with ammonia, and the bismuth was entirely precipitated at a boiling heat with a mixture of ammonium hydroxide and ammonium carbonate (in equal parts) avoiding excess, which has a solvent action upon bismuth carbonate. The precipitate, when well washed and dried, is placed upon glazed paper, the remnants of bismuth carbonate adhering to the filter are dissolved in concentrated nitric acid, the solution is evaporated in a weighed porcelain crucible to dryness and

gently ignited. It is then allowed to dry, the bulk of the precipitate is added and ignited until the weight remains constant.

Where the quantities of hydrochloric acid were small (20 or 25 c.c.), the mercurous chloride had no grey colour, but with 30 c.c. there was a considerable reduction to metal.

In presence of bismuth mercuric chloride is not completely precipitated by phosphorous acid in a nitric solution. If we use a hydrochloric solution the precipitation is perfect, but small quantities of bismuth compounds are also thrown down.

Separation of Mercury from Lead.

In case of lead the separation in a nitric solution is preferable. In a hydrochloric solution the precipitation of mercurous chloride was complete, but it was accompanied by small quantities of lead chloride.

Separation of Mercury from Arsenic.

In all experiments the arsenic was weighed out as teroxide. Two experiments were undertaken, respectively in hydrochloric and in nitric solution. The arsenic teroxide was oxidised by means of nitric acid, the solution evaporated on the water-bath nearly to dryness, and thus all the nitric acid was expelled. The mercuric chloride and the requisite quantity of acid were then added, and the operation was conducted exactly as with metals of the copper group. When hydrochloric acid was used the deposit of mercurous chloride indicated a partial reduction to the state of metal. The precipitate was found to be free from arsenical compounds.

The arsenic present in the filtrate was precipitated with hydrogen sulphide. After complete saturation the liquid was allowed to stand for 24 hours in a warm place, the precipitate was collected, sulphuretted hydrogen was again passed into the filtrate, and after prolonged standing the second deposit of arsenic sulphide was united with the main precipitate. After perforating the filter the precipitate is washed into a beaker with boiling water, to which a few c.c. of potassium sulphide and potassium hydroxide have been added, and further digested with about 20 c.c. of the above mixture until the whole is dissolved. The liquid is then diluted with water, boiled up and mixed with ammonium chloride. As there ensued no separation of mercury sulphide the arsenic was precipitated from the clear liquid as arsenic pentasulphide by acidification with hydrochloric acid. The precipitate was then collected on a filter, dissolved in hot ammonium sulphide, the solution heated in a porcelain capsule on the water-bath until the ammonium sulphide is decomposed, and the arsenic sulphide which separates out in crusts is oxidised with potassium chlorate and hydrochloric acid.

The sulphur separated out is removed by filtration, the filtrate supersaturated with ammonia, and the arsenic is precipitated as magnesium-ammonium arseniate by means of an ammoniacal solution of magnesium chloride. After standing for 24 hours the precipitate thus obtained is re-dissolved in hydrochloric acid and again precipitated with concentrated ammonia.

Separation of Mercury from Antimony.

Three experiments were made, two in a hydrochloric, and a third in a nitric solution. The antimony was weighed as teroxide after it had been slightly heated in a current of carbon dioxide and allowed to cool. The oxidation of the antimony oxide was effected by means of nitric and hydrochloric acid. The teroxide was dissolved in concentrated hydrochloric acid, and concentrated nitric acid was then gradually added until all the antimony teroxide is oxidised. The excess of nitric acid is expelled, and the liquid is evaporated almost to dryness. A little tartaric acid (1.5 grms.) is then added in order to retain the antimonious acid in solution when diluted with water. The mercuric chloride was then dissolved in water with the addition of the requisite quantity of acid. In the nitric experiment it was found necessary first to dissolve

* *Zeitschrift für Analytische Chemie*, vol. xxxiv., p. 391.

the antimonious acid in a little hydrochloric acid before adding the nitric acid. The entire liquid was then made up to 150 c.c., the phosphorous acid was added, and the operation concluded as already indicated. The results show that the separation of mercury from antimony gives good results either in a hydrochloric or in a nitric solution.

Separation of Mercury from Tin.

The experiments showed that a perfect separation of mercury from tin cannot be effected by the method in question.

Separation of Mercury from Cadmium, Bismuth, Copper, Lead, Arsenic, and Antimony.

Two analyses were effected in which only the mercury was determined; 0.2 grm. of each metal was weighed out.

Arsenic and antimony tetroxides were first oxidised by means of hydrochloric and nitric acids, and there was added a solution of cadmium oxide, copper oxide, and bismuth oxide in 20 c.c. hydrochloric acid, and the mercuric chloride. The liquid was diluted to about 130 c.c., and lastly an aqueous solution of the lead nitrate was added.

After small quantities of lead chloride deposited had been re-dissolved by a gentle heat, 10 c.c. of the solution of phosphorous acid were added, when mercurous chloride was immediately separated. After the lapse of four hours the mixture was filtered, the precipitate was washed first with concentrated hydrochloric acid in order to re-dissolve bismuth, and then with boiling water in order to re-dissolve any lead chloride which might have been separated out.

The precipitate was oxidised with hydrochloric acid and potassium chlorate, the solution precipitated with hydrogen sulphide, and the precipitate treated with the mixture of potassium sulphide and potassium hydroxide. Small portions remained undissolved. From this filtrate the mercury was precipitated as sulphide by means of ammonium chloride, purified as already described, and weighed.

The filtrate, when subsequently tested with phosphorous acid, gave no further precipitation of mercurous chloride, whence the precipitation must have been complete.

The analyses show that mercury is completely precipitated by phosphorous acid in the simultaneous presence of lead, bismuth, copper, cadmium, arsenic, and antimony. The precipitate, however, always carries down with it slight traces of other metallic compounds (bismuth and lead).

It is established by these investigations that Rose's method permits of a smooth separation of mercury from copper, cadmium, arsenic, and antimony, whether in a nitric or a hydrochloric solution. The separation of mercury ensues smoothly only in a nitric solution, since in a hydrochloric liquid lead chloride is separated out along with the mercurous chloride.

A separation of mercury from bismuth by this method is not practicable in a nitric solution, and in a hydrochloric solution it is not satisfactory, since the mercurous chloride, though completely precipitated, carries down compounds of bismuth. In presence of tin the method is not applicable, since tin tetrachloride has a solvent action upon mercurous chloride and hence prevents the complete precipitation of the mercury.

which it is mixed is well known. And the very purest lithium compounds, when put into a hydrogen flame or a Bunsen burner, show the sodium spectrum more distinctly than it is seen in the ordinary atmosphere.

This difficulty is such that MM. Bunsen, Diehl, and Troost, in their works on lithium, have reached the utmost limit of purity. In my researches on the atomic weight of lithium, I could not exceed their results. Having subsequently found that, under certain atmospheric conditions, a Bunsen burner, or pure hydrogen flame, showed no trace of the sodium spectrum, I reopened my work, and found that there is a method of obtaining a lithium compound which, when put into a non-sodic flame, no longer shows the sodium spectrum at any temperature whatever.

I found that after having made *carbonate* of lithium, by the method described in the first part of this chapter, so free from all solid bodies, and especially from *silica*, as not to show the sodium spectrum any more distinctly than it was seen in the air of the *laboratory*, it sufficed to heat it then in *pure air*, in an oxyhydrogen blowpipe, with a great excess of hydrogen, in such a manner as to melt it, and reduce it to the state of oxide of lithium. On then raising the lithium compound, in an oxyhydrogen blowpipe, less rich in hydrogen, to a temperature high enough to volatilise, in a few minutes, one-third or one-half of the amount used, according to the relative purity of the carbonate, the spectrum showed no trace of the sodium line. *The method depends, therefore, on the simultaneous application of heat and a current of gas.*

The complete separation of sodium being a very delicate operation, because it has to be carried out in platinum at a temperature very near the fusing-point of this metal, I must enter into a few details of the method I used to effect this separation and observe the phenomena produced.

I put a *concave* plate of pure platinum on a strong platinum tripod, to one side of, and the exact height of the slit in, the spectrocope. Having raised this plate to white heat, I put a quantity of carbonate of lithium on it, sufficient to fill the hollow with melted oxide of lithium.

I directed an oxyhydrogen blowpipe flame with an excess of hydrogen, on to the carbonate, by means of a platinum blowpipe, arranged in a suitable position. The mixture of gases and the pressure were previously regulated so as to give a flame 20 c.m. long, and the temperature of the upper third of which should be below that at which hydrogen becomes incandescent, and consequently *below the fusing-point of platinum.*

When heated, the carbonate melts without altering. If the temperature be then raised, it begins to boil; this lasts until all the carbonic acid is driven off from it. Oxide or hydroxide of lithium made thus is a clear, colourless, very mobile liquid, which wets platinum, and volatilises entirely if the carbonate is quite free from silicates, leaving perfectly pure platinum intact.

During the liberation of carbonic acid, spectrum analysis of either the *purple* or *red* flame showed a *faint* sodium spectrum, which quickly faded away and disappeared entirely, when *one-third*, or at most a half, of the oxide of lithium was volatilised, and left only the well-known lithium spectrum, the characteristics of which varied in proportion to the temperature and luminosity, as I shall describe further on.

When the sodium has been eliminated from the lithium in perfectly pure platinum dishes, the oxide or hydroxide left is, after cooling, in the form of a colourless, transparent glass, very friable, and soluble in water, forming a perfectly clear solution. The surface of the platinum on which it was purified is exactly the same as it was before the operation. If ordinary platinum be used, containing silicon and foreign metals, especially iron, copper, iridium, and rhodium, the lithium compound is coloured and leaves a residue, when volatilised at a temperature near the fusing-point of platinum. In this case, moreover, the

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 31.)

Spectroscopic Study of Lithium.—Characteristics given to Flames; Electric Spark, Electric Discharge, and Electric Arc by Compounds of Lithium.

The Luminous Spectra of Lithium.—The difficulty in separating a sodium salt from a lithium compound with

surface of the platinum is attacked, and the metal, having been previously treated with dilute hydrochloric acid and washed with water, gives persistent and strong signs of the presence of lithium, when re-melted in an oxyhydrogen blowpipe.

It follows from my observations, made at different times, that the products of the decomposition of carbonate of lithium by oxyhydrogen gas only attack platinum when impurities are present, as is generally the case with commercial platinum.

With oxy-coal-gas the phenomena occur in exactly the same way as with oxyhydrogen.

I return now to the spectrum of lithium under the different conditions in which I observed it. I repeat that my object was at first to find out whether it was possible to form a luminous spectrum of lithium, without seeing the double sodium line at the same time.

I profited by the considerable amount of work I did in order to obtain exceptionally pure carbonate of lithium, when studying afresh the spectrum of this metal. It was, besides, necessary for me to know this spectrum accurately, in order to find out whether it changed under the influence of a great rise of temperature, and under what circumstances this change took place.

If, directly after the oxide of lithium free from sodium solidified it were introduced into the *dark* flame of pure hydrogen, it gave it a very deep purple colour, and on spectrum analysis, a strong red line was seen at from 33 to 34 divisions on my spectroscope, corresponding to from 31.5 to 32.5 on that of M. Bunsen, and a very faint orange line at 45.5 divisions on my spectroscope, corresponding to 45.0 on that of M. Bunsen. This oxide of lithium can be completely volatilised in a long or short hydrogen flame, putting the oxide in front or at the side, without showing a single line. The flame spectrum of chloride of lithium described by M. Bunsen is similar.

On warming this oxide, on the same concave platinum plate on which it was freed from sodium, in the point of an oxy-coal-gas or oxyhydrogen blowpipe, so as to *partially* melt it, this flame also turns very deep purple; spectrum analysis of it shows nothing but a *single* deep red line. On altering the blowpipe, so as to raise the temperature, this line becomes brilliant, and, at the same time, the orange-yellow line mentioned above appears. The temperature may be raised very considerably without any other lines appearing; the only change is that the red and orange-yellow lines become more distinct.

On raising the temperature by the admission of oxygen, so as to bring the excess hydrogen to incandescence, the line originally of a reddish brown appears to become decidedly red, and the orange-yellow line pure yellow; at the same time a pale blue line becomes visible—this line was first noticed by Messrs. Frankland and Lockyer. When working as I have just described, I could never find the line mentioned by M. Lecoq de Boisbaudran, at 135.75 on the micrometer of his spectroscope. If the slit be narrow enough, the spectrum is quite *dark*, marked by the three lines mentioned above.

On raising the temperature *to the fusing-point of platinum*, and introducing into the inner cone of an oxyhydrogen blowpipe flame a small cone of powdered iridium, mixed with oxide of lithium, and attached to a carbon pencil about 1 m.m. diameter, the colour of the inner cone immediately changes to *deep blue*, the envelope of the cone becomes brownish red, and the point of the flame carmine-red. Spectrum analysis of the deep blue and brownish red light shows a very bright continuous spectrum, marked with three lines, amongst which the double sodium line and the second violet line—recently discovered by Messrs. Liveing and Dewar in the spectrum of lithium in the electric arc—are altogether wanting.

On lowering the temperature, the spectral phenomena occur in reverse order. The blue line, which appeared last, disappears first; then the orange-yellow line; and lastly the red line. But the care which I took in carrying on my observations enables me to state that during the

appearances and disappearances of the characteristic lines of oxide of lithium, I was never able to see the sodium line when working on a compound *purified* from sodium. M. Rommelaere, who gave me his earnest assistance in preparing the carbonate of lithium and carrying on these researches, found the same results as I did, when using M. Hilger's fine direct-vision spectroscope, whilst I used in succession the late M. Steinheil's and M. Duboscq's spectroscopes, fitted respectively with two and three prisms.

Sulphate of lithium showed, in a hydrogen flame or in an oxyhydrogen blowpipe, the same spectrum as oxide of lithium under the same conditions; I satisfied myself of this fact when working on sulphates prepared by M. Bunsen and by myself.

During the revision of my spectroscopic work, in collaboration with M. Depaire, we tried to ascertain together—using M. Hilger's spectroscope with two half-prisms and quartz eyepiece, instead of the large spectroscope with one prism and flint glass eyepiece, and using in succession sulphate of lithium made by M. Bunsen and chloride of lithium made by M. Depaire—whether we could see the second blue line discovered by Messrs. Liveing and Dewar in the spectrum of lithium in the inner cone of an oxy-coal-gas blowpipe.

With this object, we put the lithium compounds successively into an oxy-coal-gas blowpipe made incandescent by an excess of oxygen, and into the inner cone of this flame, by means of a fine carbon pencil which had been cleansed and recently raised to white heat. In spite of all our efforts, *we were not able to detect the second blue lithium line, which was only visible, with the same spectroscope, in the electric spark, discharge, and arc, charged with lithium*, as I shall mention farther on.

Thus there are *three flame spectra* of oxide and sulphate of lithium. The first corresponds to the fusing-point of oxide of lithium—this can be best seen in a Bunsen burner; the second corresponds to the temperature of hydrogen burning in air; and the third to the temperature at which hydrogen becomes incandescent.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 19th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. E. H. Hills, Philip J. Hartog, and Edgar S. Hanes were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. W. H. Barker, 26, Belgrave Road, Longton, Staffs.; Maurice Blood, 15, Clyde Road, Bristol; James Craig, 6, Montague Street, Gt. Western Road, Glasgow; Charles James Pemeller Fuller, Mona House, Horwich, Lancs.

Of the following papers those marked * were read:—

*151. "*The Liquefaction of Air and Research at Low Temperatures.*" By JAMES DEWAR, LL.D., F.R.S.

The author reviewed all the forms of apparatus that had been used in low temperature research, pointing out that the best and most economical plant for the production of liquid air or oxygen was one based on the general plan of the apparatus used by Pictet in his celebrated experiments on the liquefaction of oxygen in the year 1878. Instead of using Pictet's combined circuits of liquid sulphur dioxide and carbon dioxide maintained in continuous circulation by means of compression, liquefaction, and subsequent exhaustion, it has been found preferable to select ethylene after Cailletet and Wroblewski, for one

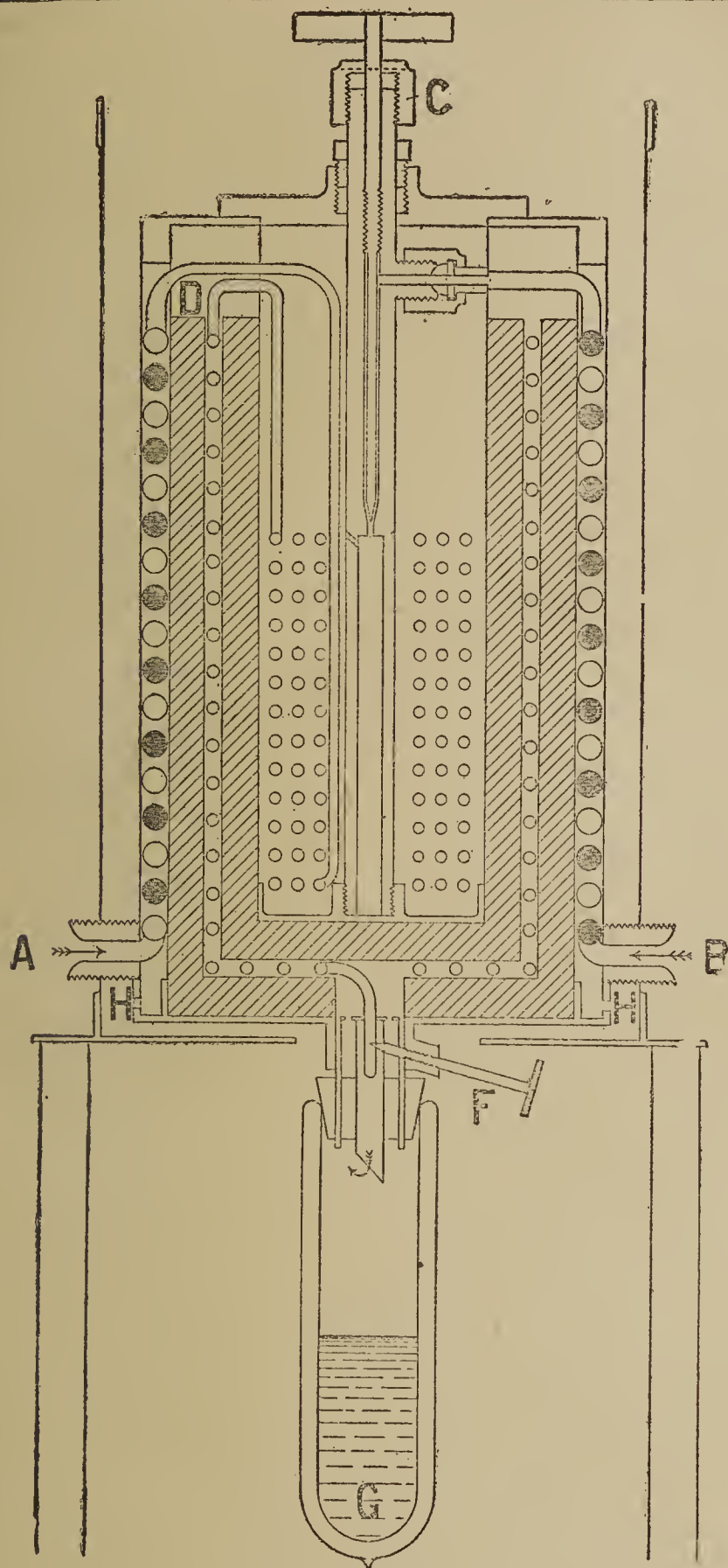


FIG. 1.

A, air or oxygen inlet; B, carbon dioxide inlet; C, carbon dioxide valve; D, regenerator coils; E, air or oxygen expansion valve; G, vacuum vessel with liquid oxygen; H, carbon dioxide and air outlet; O, air coil; ●, carbon dioxide coil.

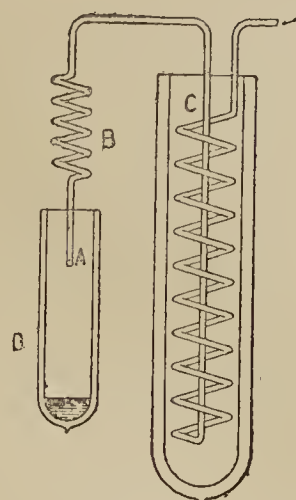


FIG. 2.

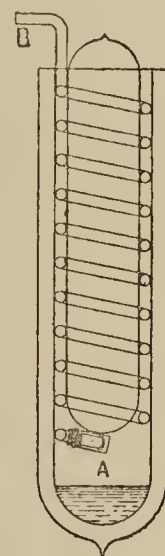


FIG. 3.



FIG. 4.

circuit, and to join with it either nitrous oxide, or, better, carbon dioxide. Further, instead of making the oxygen to be liquefied by heating potassium chlorate in an iron bomb directly connected with the refrigerator, and thereby

reaching high gas pressures, it has been found more convenient to use gas previously compressed in steel cylinders. The stopcock that Pictet employed to draw off liquid and produce sudden expansion was in his apparatus placed

outside the refrigerator proper, but it is now placed inside, so as to be kept cool by the gases undergoing expansion. This improvement was introduced along with that of isolating the liquid gases by surrounding them with their own vapour in the apparatus made wholly of copper, described and figured in the *Proc. Roy. Inst.* for 1886. In all continuously working circuits of liquid gases used in refrigerating apparatus the regenerative principle applied to cold first introduced by Siemens, in 1857, and subsequently employed in the freezing machines of Kirk, Coleman, Solvay, Linde, and others has been adopted. Quite independently, Professor Kamerlingh Onnes, of Leiden, has used the regenerative principle in the construction of the cooling circuits in his cryogenic laboratory (see paper by Dr. H. Kamerlingh Onnes, on the "Cryogenic Laboratory at Leiden, and on the Production of very Low Temperatures," Amsterdam Akademie, 1894). Apart, therefore, from important mechanical details, and the conduct of the general working, nothing new has been added by any investigator to the principles involved in the construction and use of low temperature apparatus since the year 1878. The *Phil. Mag.* of February, 1895, contains a fantastic claim put forward by Professor Olszewski, of Cracow, that because he used in 1890 a steel tube combined with a stopcock to draw off liquid oxygen, he had taught the world, to use his own language, "the method of getting large quantities of liquid gases." But when, in addition, Olszewski alleges, four years after the event, that the experiments made at the Royal Institution since 1891 are chiefly borrowed from Cracow, and that he is entitled to the credit of all low temperature research subsequent to 1891, because of his steel tube and stopcock invention, one can only wonder at the meagre additions to knowledge that in our time are unhesitatingly brought forward as original, and more especially that scientific men could be got to give them any currency in this country. Such persons should read the late Professor Wroblewski's pamphlet entitled "Comment l'air a été Liquefié" (Paris, Librairie du Luxembourg, 1885), and make themselves generally acquainted with his work before coming to hasty conclusions on claims of priority brought forward by the Professor of Chemistry at Cracow.

Liquefying Apparatus.—The author proceeded to describe the construction and show the working of a laboratory apparatus for the production of liquid oxygen and other gases, represented in section (Fig. 1). With this simple arrangement 100 c.c. of liquid oxygen can readily be obtained, the cooling agent being carbon dioxide, at the temperature of -79° , no exhaustion being used. The gaseous oxygen, cooled before expansion by passing through a spiral of copper tube immersed in solid carbon dioxide, passes through a fine screw stopcock under a pressure of 100 atmos., and thence backwards over the coils of pipe. The liquid oxygen begins to drop in about a quarter of an hour from starting. The general arrangement of the circuits will be easily understood from the sectional drawing. The pressure in the oxygen cylinders at starting is generally about 150 atmos., and the best results are got by working down to about 100°. This little apparatus will enable liquid oxygen to be used for demonstration and research in all laboratories.

Vacuum Vessels.—It has been shown in previous papers* that a good exhaustion reduces the influx of heat to one-fifth part of what is conveyed when the annular space in such double-walled vacuum vessels is filled with air. If the interior walls are silvered, or excess of mercury is left in the vessel, the influx of heat is diminished to one-sixth part of the amount entering without the metallic coating. The total effect of the high vacuum and silvering is to reduce the ingoing heat to 1/30th part, or, roughly, 3½ per cent. Vessels constructed with three dry air spaces only reduced the influx of heat to 35 per cent. An ordinary mercury vacuum vessel is therefore ten times more

economical for storing liquid air, apart from considerations of manipulation, than a triple annular-spaced air vessel. It has been suggested that the metallic coating of mercury does no good, because Pictet has found that all kinds of matter at low temperatures become transparent to heat. The results above mentioned dispose of this assumption, and direct experiment proves that no increase in the transparency of glass to thermal radiation takes place by cooling to the boiling-point of air.*

Solid Air.—As Professor Olszewski has recently alleged that air does not solidify at the lowest pressures (*Phil. Mag.*, February, 1895), the author's former experiments were repeated on a larger scale. If a litre of liquid air is placed in a globular silvered vacuum vessel and subjected to exhaustion, as much as half a litre of solid air can be obtained and maintained in this condition for half an hour. At first the solid is a stiff, transparent jelly, which, when examined in the magnetic field, has the liquid oxygen drawn out of it to the poles. This proves that solid air is a nitrogen-jelly containing liquid oxygen. Solid air can only be examined in a vacuum or in an atmosphere of hydrogen, because it instantly melts on exposure to the air, giving rise to the liquefaction of an additional quantity of air. It is strange to see a mass of solid air melting in contact with the atmosphere, and all the time welling up like a kind of fountain.

Samples of Air Liquefied in Sealed Flasks.—In a previous paper "On the Relative Behaviour of Chemically Prepared and of Atmospheric Nitrogen" (*Proc. Chem. Soc.*, December, 1894) the plan of manipulating such samples was described. Two flasks of dry air that had stood over phosphoric anhydride were liquefied side by side, the only difference between the samples being that one was free from carbonic acid. The one gave a liquid that was perfectly clear, the other was turbid from the 0.04 per cent of carbon dioxide. The temperature was now lowered by further exhaustion of the liquid air surrounding the tubes until both liquids became solid. The flasks were then sealed off for the purpose of examining the composition of the air that had not been condensed. The one sample contained oxygen, 21.19 per cent, and the other 20.7 per cent. This is an additional proof to the one previously given, that, substantially, the oxygen and nitrogen in air liquefy simultaneously, even under gradually diminishing pressure, and that in these experiments all the known constituents of air are condensed together. These results finally disproved the view expressed in "A System of Inorganic Chemistry" 1891, p. 70, by Professor Ramsay, where he says: "Air has been liquefied by cooling to -192° , but as oxygen and nitrogen have not the same boiling-points, the less volatile oxygen doubtless liquefies first." In the author's former experiments, the substance now known as argon, became solid before nitrogen, but chemical nitrogen and air nitrogen, with its 0.1 per cent of argon, behaved in substantially the same way on liquefaction.

Liquid Nitric Oxide.—Great interest attaches to the behaviour of nitric oxide at low temperatures. Professor Olszewski has examined the liquid and describes it as colourless. Dr. Scott has prepared in different ways samples of nitric oxide. These have been transferred to liquefaction flasks, where they were left in contact with potash, sulphuric acid, or phosphoric acid for many days before use. Each of the samples, when cooled, gave a nearly white solid, melting into a blue liquid. The colour is more marked at the melting-point than at the boiling-point. Liquid nitric oxide is not magnetic; neither is the solid phosphorescent. Colour in the oxides

* "On Liquid Atmospheric Air," *Proc. Roy. Inst.*, 1893; "Scientific Uses of Liquid Air," *Ibid.*, 1894.

* As this is passing through the press, I observe that M. Cailliet, at the last meeting of the French Academy (*Comptes Rendus*), presented a paper by M. Solvay of Brussels, in which my device of vacuum vessels is attributed to M. Cailliet, and tacitly accepted by him! In 1873 I had already used a highly exhausted vessel of similar shape to the vacuous test-tube, in calorimetric experiments. See paper on "The Physical Constants of Hydrogenium," *Trans. Roy. Soc. Ed.*, vol. xxvii.

of nitrogen evidently begins with the second oxide. Solid nitric oxide does not show any chemical action in liquid oxygen, provided the tube containing it is completely immersed; but if the tube full of liquid oxygen is lifted into the air, almost instantly a violent explosion takes place.

Specific Gravities taken in Liquid Oxygen.—In a good vacuum vessel specific gravities may be taken in liquid oxygen with as great ease as in water.

Some twenty substances were weighed in liquid oxygen, and the apparent relative density of the oxygen determined. The results were then corrected, using Fizeau's values for the variation of the coefficient of expansion of the solids employed, and thereby the real density of liquid oxygen calculated. The resulting value was 1.1375, bar. 766.5, in the case of such different substances as cadmium, silver, lead, copper, silver iodide, calc-spar, rock crystal. Direct determinations with an exhausted glass cylindrical vessel displacing about 22 c.c. gave 1.1378. Fizeau's parabolic law for the variation of the coefficient of expansion holds down to -183° . The solid which showed the greatest contraction was a block of compressed iodine, the one that contracted least being a compressed cylinder of silver iodide. Wroblewski gave the density of liquid oxygen at the boiling-point as 1.168, whereas Olszewski found 1.124. The variation of density is about ± 0.0012 , for 20 m.m. barometric pressure. Much work requires to be done in the accurate determination of the physical constants of liquid gases.

Liquid Air.—A large silver ball weighed in liquid air gave the density of the latter as 0.910, and the corresponding density of nitrogen at its boiling-point 0.850. It is difficult to be quite certain that the constituents of liquid air are in the same proportion as the gaseous ones, so that further experiments must be made. Liquid air kept in a silvered vacuum vessel gradually rises in boiling-point from the instant of its collection, the rate of increase during the first hour being nearly directly proportional to the time. As the increase amounted to 1° in ten minutes the boiling-point of oxygen ought to have been reached within two hours. The density of liquid air, however, does not reach that of pure oxygen even after thirty hours' storage. The large apparatus can be arranged to deliver liquid air containing 49 per cent of oxygen, which gives off gas containing 20 per cent of oxygen, rising after six hours to 72.6 per cent.

Combustion in Liquid Oxygen.—A small ignited jet of hydrogen burns continuously below the surface of liquid oxygen, all the water produced being carried away as snow. There is a considerable amount of ozone formed, which concentrates as the liquid oxygen evaporates. In the same way graphite or diamond, when properly ignited, burns continuously on the surface of liquid oxygen, producing solid carbonic acid and generating ozone. If liquid oxygen is absorbed in wood charcoal, or cotton wool, and a part of the body heated to redness, combustion can start with explosive violence.

Gas Jets containing Liquid.—The experiments of Joule and Thomson and Regnault on the temperature of gas jets issuing under low pressures are well known. The following observations refer to the pressure required to produce a lowering of temperature sufficient to yield liquid in the gas jet.

The apparatus used in the study of highly compressed gas jets is represented in Fig. 2; where C is a vacuum tube which holds a coil of pipe about 5 m.m. in diameter along with carbon dioxide or liquid air for cooling the gas before expansion, and A is a small hole in the silver or copper tube about $\frac{1}{8}$ m.m. in diameter, which takes the place of a stopcock. When carbon dioxide gas at a pressure of 30 or 40 atmos. is expanded through such an aperture, liquid can be seen where the jet impinges on the wall of the vacuum tube along with a considerable amount of solid. If oxygen gas escapes from the small hole at the pressure of 100 atmos., having been cooled previously to -79° in the vessel C, a liquid jet is just visible. It is interesting to note in passing that Pictet could get no

liquid oxygen jet below 270 atmos. This was due to his stopcock being massive and outside the refrigerator. If the oxygen is replaced by air no liquid jet can be seen unless the pressure is raised to 180 atmos. If the carbon dioxide is cooled by exhaustion (to about 1 m.m. pressure) or -115 , then liquid air can easily be collected in the small vacuum vessel D, or if the air pressure is raised above 200 atmos., keeping the cooling at -79° as before. The chief difficulty is in collecting the liquid owing to the rapid current of gas. The amount of liquid in the gas jet is small and its collection is greatly facilitated by directing the spray on a part of the metallic tube above the little hole or by increasing resistance to the escaping gas by placing some few turns of the tube, like B in the figure, in the upper portion of the vacuum tube, or generally by pushing in more tube in any form. A vacuum vessel shaped like an egg-glass also works well. This practically economises the cool gas which is escaping to reduce the temperature of the gas before expansion, or, in other words, it is the cold regenerative principle. Coleman pointed out long ago that his air machine could be adapted to deliver air at as low a temperature as has yet been produced in physical research. Both Solvay and Linde have taken patents for the production of liquid air by the application of cold regeneration, but the latter has the credit of having succeeded in constructing an industrial apparatus (the plans of which are not yet published) that is lowered in temperature to -140° , or to the critical point of air in about fifteen hours, and from which liquid air containing 70 per cent oxygen is collected after that time.

For better isolation, the pipe can be rolled between two vacuum tubes, the outer one being about 9 inches long and $1\frac{1}{2}$ inch diameter, as shown in Fig. 3. The aperture in the metal pipe has a little piece of glass tube over it which helps the collection of the liquid. With such a simple apparatus and an air supply of 200 atmos. with no previous cooling, liquid air begins to collect in about five minutes, but the liquid jet can be seen in between two and three minutes. It is not advisable to work below 100 atmospheres.

In Fig. 4 the metallic tube in the vacuum vessel is placed in horizontal rings, leaving a central tube to allow the glass tube C to pass, which is used to cool bodies or examine gases under compression. The inner tube can be filled for an inch with liquid air under a pressure of 60 atmos. in about three minutes. Generally, in the experiments, about $\frac{1}{2}$ to 4 cubic feet of air passes through the different sized needle holes per minute when the pressure is about 200 atmos. As the small hole is apt to get stopped, for general working it is better to use a needle stopcock, worked from the outside by a screw passing through the middle of the coil of pipe. A double coil of pipe has advantages in the conduct of some experiments. The efficiency is small, not exceeding the liquefaction of 2 to 5 per cent of the air passing, but it is a quick method of reaching low temperatures and easy to use for cooling tubes and collecting a few hundred c.c. of liquid air, especially if the compressed air is delivered at the temperature of -79° before expansion. With larger vacuum vessels and larger regenerating coils, no doubt the yield of liquid could be increased. The liquid air resulting from the use of this form of apparatus contains about 50 per cent of oxygen. If the air is cooled with solid carbonic acid previous to its reaching the vacuum tube coil of pipe, the only change is to reduce the percentage of oxygen to 40. Successive samples of liquid taken during the working had nearly the same composition. If the arrangement shown in Fig. 2 is used, with silver tube, about $\frac{1}{16}$ in. bore, and a foot or two coiled in upper part of the vacuum vessel, liquid air containing 25 per cent of oxygen was obtained. On the other hand, the percentage of oxygen can be increased by a slight change in the mode of working.

In the above experiments air is taken at the ordinary temperature, which is a little above twice its critical tem-

perature, and is partially transformed in a period of time which, in my experiments, has never exceeded ten minutes, simply and expeditiously into the liquid state at its boiling-point, -194° , or a fall of more than 200° has been effected in this short period of time.

Experiments on Hydrogen.—Wroblewski made the first conclusive experiments on the liquefaction of hydrogen in January, 1884. He found that the gas cooled in a tube to the boiling-point of oxygen, and expanded quickly from 100 to 1 atmos., showed the same appearance of sudden ebullition as Cailletet had seen in his early oxygen experiments. No sooner had the announcement been made than Olszewski confirmed the result by expanding hydrogen from 190 atmos., previously cooled with oxygen and nitrogen in a vacuum. Olszewski declared in 1884 that he saw colourless drops, and by partial expansion to 40 atmos. the liquid hydrogen was seen by him running down the tube. Wroblewski could not confirm these results, his hydrogen being always what he called a "liquide dynamique." He proposed to get "static" liquid hydrogen by the use of hydrogen gas as a cooling agent. From this time until his death, in the year 1888, Wroblewski devoted his time to a laborious research on the isothermals of hydrogen at low temperatures. The data thus arrived at enabled him, by the use of Van der Waal's formulæ, to define the critical constants of hydrogen, its boiling-point, density, &c., and the subsequent experiments of Olszewski have confirmed the accuracy of the results. In a paper published in the *Phil. Mag.*, September, 1884, "On the Liquefaction of Oxygen and the Critical Volumes of Fluids," the suggestion was made that the critical pressure of hydrogen was wrong, and that instead of being 99 atmos. (as deduced by Sarrau from Amagat's isothermals) the gas had probably an abnormally low value for this constant. This view was substantially confirmed by Wroblewski finding a critical pressure of 13.3 atmos., or about one-fourth that of oxygen. The *CHEMICAL NEWS* (September 7, 1894) contains an account of the stage the author's hydrogen experiments had reached at that date. The object was to collect liquid hydrogen at its boiling-point, in an open vacuum vessel, which is a much more difficult problem than seeing the liquid in a glass tube under pressure and at a higher temperature. In order to raise the critical point of hydrogen to about -200° from 2 to 5 per cent of nitrogen or air was mixed with it. This is simply making an artificial gas containing a large proportion of hydrogen, which is capable of liquefaction by the use of liquid air. The results are summed up in the following extract from the paper:—"One thing can, however, be proved by the use of the gaseous mixture of hydrogen and nitrogen, viz., that by subjecting it to a high compression at a temperature of -200° and expanding the resulting liquid into air, a much lower temperature than anything that has been recorded up to the present time can be reached. This is proved by the fact that such a mixed gas gives, under the conditions, a paste or jelly of solid nitrogen, evidently giving off hydrogen because the gas coming off burns fiercely. Even when hydrogen containing only some 2 to 5 per cent of air is similarly treated the result is a white solid matter (solid air) along with a clear liquid of low density, which is so exceedingly volatile that no known device for collecting has been successful."

In Professor Olszewski's paper "On the Liquefaction of Gas" (*Phil. Mag.*, 1895), after detailing the results of his hydrogen experiments, he says: "The reason for which it has not hitherto been possible to liquefy hydrogen in a static state, is that there exists no gas having a density between that of hydrogen and nitrogen, and which might be, for instance, 7-10 ($H=1$). Such a gas would be liquefied by means of liquid oxygen or air as cooling agent, and afterwards used as a recognised menstruum in the liquefaction of hydrogen." Science will probably have to wait a very long time before this suggestion of how to get "static" liquid hydrogen is realised. The proposal Wroblewski made in 1884 of using the expansion of hy-

drogen as a cooling agent to effect the change of state is far more direct and practicable.

Liquid Hydrogen Jet and Solid Oxygen.—Hydrogen, cooled to -194° (80° abs. *t.*) the boiling-point of air, is still at a temperature which is two and a half times its critical temperature, and its direct liquefaction at this point would be comparable to that of air taken at 60° , and liquefied by the apparatus just described. Now, air supplied at such a high temperature greatly increases the difficulty and the time required for liquefaction. Still, it can be done, even with the air supply at 100° , in the course of seven minutes, and this is the best proof that hydrogen, if placed under really analogous conditions, at -194° must also liquefy with the same form of apparatus. Hydrogen, cooled to -200° , was forced through a fine nozzle under 140 atmos. pressure, and yet no liquid jet could be seen. If the hydrogen contained a few per cent of oxygen the gas jet was visible, and the liquid collected, which was chiefly oxygen, contained hydrogen in solution, the gas given off for some time being explosive.

If, however, hydrogen, previously cooled by a bath of boiling air, is allowed to expand at 200 atmos. over a regenerative coil similar to that shown in Fig. 2, but longer, a liquid jet can be seen after the circulation has continued for a few minutes along with a liquid which is in rapid rotation in the lower part of the vacuum vessel. The liquid did not accumulate, owing to its low specific gravity and the rapid current of gas. These difficulties will doubtless be overcome by the use of a differently shaped vacuum vessel and by better isolation. The liquid jet can, however, be used as a cooling agent like the spray of liquid air obtained under similar circumstances, and, this being practicable, the only difficulty is one of expense. In order to test, in the first instance, what the hydrogen jet could do in the production of lower temperatures, liquid air and oxygen were placed in the lower part of the vacuum tube just covering the jet. The result was that in a few minutes about 50 c.c. of the respective liquids were transformed into hard white solids resembling avalanche snow, quite different in appearance from the jelly-like mass of solid air got by the use of the air-pump. The solid oxygen had a pale bluish colour, showing by reflection all the absorption-bands of the liquid. The temperatures reached, and other matters, will be dealt with in a separate communication. There is no reason why a spray of liquid hydrogen, at its boiling-point in an open vacuum vessel, should not be used as a cooling agent in order to study the properties of matter at some 20° or 30° above the absolute zero. The sole difficulty is the cost.

Fluorine.—This is the only widely-distributed element that has not been liquefied. Some years ago Wallach and Hensler pointed out that an examination of the boiling-points of substituted halogen organic compounds led to the conclusion that, although the atomic weight of fluorine is 19 times that of hydrogen, yet it must in the free state approach hydrogen in volatility. This view is confirmed by the specific refractive index which Gladstone showed was rather lower than hydrogen. If the chemical energy of fluorine at low temperatures is abolished like that of other active substances, then some kind of glass or other transparent material not so brittle as calcium fluoride could be employed in the form of a tube, and its liquefaction achieved by the use of hydrogen as a cooling agent.

During the conduct of these investigations, able assistance has been rendered by Mr. Robert Lennox, whose name has been so often mentioned in the Royal Institution lectures. Valuable help has also been given by Mr. J. W. Heath, Assistant at the Royal Institution.

DISCUSSION.

Professor RAMSAY remarked that Professor Olszewski had succeeded in liquefying hydrogen, and from unpublished information received from Cracow, he was able to state that a fair amount of liquid had been obtained, not

as a froth, but in a state of quiet ebullition, by surrounding a tube containing compressed hydrogen by another tube also containing compressed hydrogen at the temperature of oxygen boiling at a very low pressure. On allowing the hydrogen in the middle jacket suddenly to expand, the hydrogen in the innermost tube liquefied, and was seen to have a meniscus. Its critical point and its boiling-point, under atmospheric pressure, were determined by means of a resistance thermometer. There would appear to be no difficulty in distinguishing the meniscus of hydrogen, where the liquid is 50 times as heavy as the gas, for it is perfectly easy to see a meniscus with such a liquid as ether, at temperatures so near the critical point that the liquid has only three or four times the density of the gas.

Mr. BLOUNT said that the first account of the Linde process for liquefying air had been published in the early autumn of 1895, in the form of a paper read by Herr Schrötter before the Association of German Engineers at Aachen. Briefly, it consisted in taking advantage of the fact that air, not being a perfect gas, is permanently cooled when allowed to expand through a narrow opening without doing external work. The lowering of temperature was expressed by Joule and Thomson's formula,—

$$t = \frac{p_2 - p_1}{4} \left(\frac{289}{T_1} \right)$$

where t is the fall in temperature in degrees centigrade, p_2 is the pressure of the air before it passes the opening, p_1 is the pressure of the air after passing the opening, and T_1 is the absolute temperature of the air before passing the opening. The effect was made cumulative by causing the air thus cooled to cool that which was about to pass through the opening. This was effected by the use of two long concentric tubes, the inner conveying the air to be cooled, and the annular space between the two being traversed by the cooling air. Circulation was maintained by means of an ordinary air compressor, and the temperature fell until the critical temperature was reached. A subsidiary compressor supplied fresh air to the cycle to replace that liquefied. The process was interesting because it differed fundamentally from those usually employed for the liquefaction of difficultly condensable gases, in two respects, viz. (1) it dispensed with the use of intermediate cooling agents, and (2) it applied a method for the cumulative withdrawal of heat analogous to the converse process of heat regeneration. Trials of the process had been made on a considerable scale, and there appeared to be no difficulty in liquefying air cheaply and in quantity.

Lord PLAYFAIR said, as a Past-President of the Society he was aware that it is not the practice to move a vote of thanks to the reader of a paper, so that he must not conclude with a motion to that effect. But he was sure that he was expressing the sentiments of all present, when he said that they were grateful for the admirable exposition and splendid experiments which they had heard and seen. It is known to them all that an undesirable controversy had been going on as to how much originality there is in the researches of Professor Dewar, whom he had the honour of claiming as an old student and assistant when he was Professor in Edinburgh. He had wasted his time in reading these attacks, and they have had no influence on his mind, or rather that they had influenced him to send a subscription to the Royal Institution towards the cost of the apparatus. The diagram of Pictet's apparatus, now shown, certainly gives to the general chemist the most original conceptions as to how the problem of liquefying gases should be attacked. But if Pictet were now with them, and could see the great advances which had been made on his ideas, he would be the first to recognise their importance, and to congratulate Professor Dewar. It is only in mythology that Minerva, full grown, and panoplied in complete armour, is born from the brain of Jupiter after a prolonged gestation. In human

brains one discovery suggests another, and we proceed to the goal of knowledge step by step. The world now feels that Watt's discoveries, in improving the steam-engine, gave an enormous impulse to civilisation. But the men of his day were petty enough to deny him merit, and they went to a court of justice to prove that every one of his discoveries had previously been made by other men, and, more strange still, the court agreed with them and solemnly declared that Watt had done nothing to improve the steam-engine. Every discovery can be connected with previous discoveries. Would the merit of Rayleigh and Ramsay be lessened as the discoverers of argon because Cavendish had it undoubtedly as the residue in his tube in his famous experiment on air? It is to be hoped that Professor Dewar will go on with his magnificent experiments on the liquefaction of gases, and with the researches which come from them, without caring for the mosquitoes of science which buzz about his ears.

Dr. ARMSTRONG said that, after what had fallen from Lord Playfair, he would venture to express the opinion that the attacks made on Professor Dewar during the past few months were disgraceful. In these days we should encourage as far as possible all who were engaged in such dangerous and difficult work, not decry their labours. The history of the Royal Institution in the past, in so far as concerned the liquefaction of gases, was a glorious one, and he had no doubt that when the work done there more recently came to be considered without prejudice, it would be regarded as equally important. In fact there was evidence of this already. Professor Onnes, of Leiden, who, with most limited appliances and means, had already accomplished so much in the field of research at low temperatures,—an acknowledged expert in these matters,—in a recent publication, in which justice was done to all workers, clearly recognised that much credit was due to Professor Dewar for his various improvements. He did not consider it necessary to thank Professor Dewar, but thought that his assistants should not be forgotten. Messrs. Lennox and Heath had done much service in connection with the work generally, and especially in making the present demonstration possible.

Professor DEWAR, in reply, stated that he could have no knowledge of unpublished work on the liquefaction of hydrogen. The mere fact of liquefaction was first definitely given by Wroblewski, although Cailletet had made an earlier experiment of the same kind. His paper contained a quotation from Prof. Olszewski's communication made to the *Philosophical Magazine* in Feb., 1895, in which Olszewski distinctly says that he had not succeeded in getting liquid hydrogen in the "static" condition. Further, in a later paper, published in the same journal, for August, 1895, no mention is made of getting a "fair amount of liquid in a state of quiet ebullition" or of seeing a "meniscus." Even the method of working, to which reference has been made, is not mentioned, far less the result of the experiments made by the speaker in 1894. He was unable to understand why such a point should be made of seeing a meniscus, considering that the liquid can be seen. The remarks about the difficulty of separating liquid hydrogen from the gas had reference to a fine rain of fluid in a rapidly rushing stream of gas passing through vacuum vessels, and has no relation whatever to critical point phenomena to which reference had been made. If the liquid oxygen and air-jets shown have any resemblance to the Linde apparatus described by Mr. Blount, chemists, for once, may be congratulated that a small laboratory apparatus works in some respects better than a large industrial plant. The Linde apparatus after working fifteen hours is capable of reducing the temperature of air to its critical point, whereas in the present small apparatus liquid air is produced in five minutes. Such a process cannot replace the use of "cooling agents" when considerable quantities of liquid air have to be produced in a short period of time as in ordinary laboratory work. It is a mistake to attribute to

Linde the idea of using the "cumulative withdrawal of heat," for the first time, in his apparatus; but he has succeeded in making a workable industrial machine, and that is a very important step. The late Professor Wroblewski, as early as the year 1884, predicted that liquid air would be the refrigerating agent of the future; his prophecy seems about to be realised.

(To be continued).

NOTICES OF BOOKS.

L'Eau Potable. ("Potable Water"). By FRANÇOIS COREIL. Paris: J. B. Baillière et Fils. 1896. 16mo., pp. 359.

THE present volume is one of the series of important works issued by Messrs. J. B. Baillière and Son under the general title "Encyclopédie de Chimie Industrielle." It may justly take a very high rank among the hygienic writings of the day.

After an Introduction, in which the author recognises that water is still the true king of non-intoxicating beverages, M. Coreil treats of its elements, normal and accidental or injurious. On the effects of waters rich in mineral impurities we find no certain decision. The statistics collected by Letheby, who finds that in sixty-five British towns these mineral matters are found in proportions inversely as the death-rates, are vitiated by the fact that the cities supplied with pure water—such as Glasgow, Manchester, Leeds, Sheffield, &c.—are precisely those which suffer from over-crowding, unhealthy occupations, and polluted atmospheres. As regards organic pollutions, the author insists that a water cannot produce any given malady unless it has received the pathogenic germs of such malady.

A quotation shows that even Hippocrates was fully aware of the sanitary or anti-sanitary influence of the water-supply, and of its correction. Nevertheless it is still a debated question whether diseases are more due to the water actually drunk or to that stagnating below the soil (*Trink-wasser* and *Grund-wasser theorie* of German hygienists). In a passage here quoted, from a German engineer of the name of Grahn, it is asserted that so long as Birmingham was supplied with the dirty water of the Thames (*sic!*) it was one of the healthiest of large cities, but since it has begun to consume the pure water from the springs of the red sandstone its mortality has been increasing daily. On the contrary, observations made in France lead to more intelligible results, and are more in conformity with what might be expected.

In a very interesting chapter M. Coreil examines the influence of impure waters in a number of diseases—goitre, dysentery, calcular affections, malaria, jaundice, typhoid fever, and especially cholera.

The presence of animal parasites—such as the *Medina* worm, the larvæ of *Bilharzia hematobia*, and the earlier stages of tapeworm—are also traced to the use of impure waters. The author has omitted to mention that the occurrence of hydatidous cysts is due to water polluted by the excretions and secretions of dogs, which are the "intermediate hosts" of some species of tænia.

In treating of the sources of drinking-water,—such as rain, snow, springs, rivers, wells, &c.,—the author shows very clearly how the water of a stream becomes gradually polluted as it traverses a populous and cultivated region. One error seems to have escaped him: he mentions (p. 46) that the higher vegetation (such as water-cress and reeds) gradually give place to Algæ and bacteria. Now Slater has shown by experiment that water-cress flourishes most luxuriantly in foul, unpurified sewage. M. Coreil admits the self-purification of rivers as a fact, but he omits to mention, among the agencies of this improvement, the nascent oxygen given off from the leaves of aquatic vegetation.

The second part of the work is devoted to the chemical analysis of waters, including the taking of samples. The official questions which must be replied to by any community about to introduce a new water-supply are exceedingly judicious, and might well be adopted in Britain.

Then follow the methods for chemical analysis, qualitative and quantitative.

For the recognition of nitrates we find described the brucine and diphenylamine processes, and that with sulphuric acid and phenol. The methods recommended for the detection of nitrites are those of Schönbein, Trommsdorff, and Griess. For determining albumenoid ammonia we find the method known as that of Wanklyn and Chapman.

Our space unfortunately does not allow us to abstract the instructions given for the microscopic and microbiological examination of waters. It must suffice for us to say that the directions given are most elaborate, and are accompanied with a description of the principal morbid species.

This work should be added to the library of every hygienic chemist.

A Manual of Inorganic Chemistry. By T. E. THORPE, B.Sc., Ph.D., Sc.D., LL.D., F.R.S. London and Glasgow: Collins, Sons, and Co. (Ltd.) 1896. Vol. I. The Non-Metals, pp. 511. Vol. II.—The Metals, pp. 430.

AS regards extent this work occupies a useful medium position between such bulky and necessarily expensive works as those of L. Gmelin, Roscoe, and Schorlemmer, and a few others of similar rank, and the meagre handbooks written in accordance with some "syllabus."

Dr. Thorpe has brought down his subject to the level of the most recent discoveries. We have a full account of argon as at present ascertained. Helium figures as a Supplement to Vol. I. The less-known elements, such as the metals of the rare earths, and gallium and germanium, are carefully described. Spectral analysis and electro-chemical decomposition form the subject of a chapter in the second volume. Fluorine is frankly placed at the head of the halogens. Hydrazine and its compounds, and cyanogen, are included in the inorganic part of the Science.

The present number of the elements is given a 75 to 80. They are distinctly regarded as provisional, though the author indulges in no speculations concerning their origin or any previous or future state of matter. The Periodic Law figures in the first chapter of Vol. II.

This work must be recommended for senior students. They will find here no important class of phenomena ignored, and they will not learn from the author anything which they will need to unlearn in their after career. Dr. Thorpe's work is also of no small merit as a work of reference.

The Chemistry of Pottery. By KARL LANGENBECK, Superintendent of the Mosaic Tile Company, formerly Superintendent of Rookwood Pottery, Chemist to the American Encaustic Tiling Co., &c. Eastern Pennsylvania: Chemical Publishing Co. 1895. Pp. 197.

WE can scarcely admit the assertion conveyed in the author's Preface, viz., "that the pottery industries of England have afforded chemists little opportunity for systematic work, so that they have remained largely on an empirical basis, and have supplied nothing of moment to chemical technology." We have lived under the impression that systematic experimental work had been a main feature in the establishments of Wedgwood in the past and of Doulton in the present. The work before us can scarcely be regarded as written in idiomatic English. "Unlocking" clays or other minerals is an expression apt to puzzle readers who are not German scholars.

The art of sampling the raw materials, and the ne-

cessity for its correct performance, have been painfully brought under the notice of every chemist who has had to analyse specimens not fairly characteristic of the bulk which they profess to represent. The regulation of temperatures by means of Seger's pyrometric cones will doubtless have found almost universal adoption.

The author is justifiably severe upon receipts founded on analyses which, if carefully and accurately executed, take no account of the temperatures to be employed.

As regards glazes, Mr. Langenbeck seems to give a preference to those containing lead. That they are very widely employed—indeed to a predominating degree—must be admitted; but they are so generally, strongly, and justly objected to on hygienic grounds, that one of the chief duties of the ceramic chemist should be their supercession by some safe composition.

The work before us, though of course written with a predominating regard to American materials, will be of use to British ceramic industrialists.

CORRESPONDENCE.

ESTIMATION OF INSOLUBLE PHOSPHATE.

To the Editor of the Chemical News.

SIR,—With reference to a "Note on the Rapid Estimation of Insoluble Phosphate," by Mr. Vincent Edwards (CHEMICAL NEWS, vol. lxxiii., p. 25), I do not think that the process would work out with a very great degree of accuracy, for the following reasons:—

When the solution of "insoluble phosphate" in HCl is neutralised and made alkaline with ammonia, and the acetic acid added, a certain proportion of the phosphoric acid would be precipitated in combination with the iron and alumina present. The phosphates of iron and alumina so precipitated are not of constant composition, containing varying quantities or percentages of phosphoric acid. Freshly precipitated phosphates of iron and alumina are only partially acted upon by standard solutions of uranium acetate or nitrate, and even when so acted upon they behave in a very inconstant manner.

Under these circumstances, this proposed volumetric process would give very uncertain results, and could hardly compete with the old gravimetric process except for very rough results. The following is the best method of which the writer is aware for the rapid estimation of the insoluble phosphate in "supers" and other dissolved manures, which, though not strictly accurate, gives results very near to the truth, quite sufficiently so for most work's laboratories. The process is, of course, quite old and well known, but perhaps there may be no harm in reproducing it here:—

Weigh 1 or 2 grms. of the substance to be examined; wash out the soluble phosphate in usual way, with first cold and then hot water; collect the insoluble residue on a filter, and wash with hot water; transfer the residue from the filter back into the beaker, add strong HCl, digest on sand-bath until all the phosphate has dissolved, add a small quantity of hot water; filter off the sand and insoluble matters, wash with hot water, put the filtrate on sand-bath and raise to boiling; add strong ammonia in excess. Filter off the precipitate, wash twice with hot water, stirring up the precipitate each time with the jet; dissolve the precipitate off the filter-paper back into the beaker with dilute HCl (1 in 4). Raise to boiling again, add strong ammonia in excess, filter off, dry, burn, and weigh as the insoluble phosphate.

The amount of substance advised to be taken by Mr. Edwards for his process appears to me to be rather small for an estimation of this kind, and might prove another source of error.—I am, &c.,

GEO. H. ALLIBON.

Messrs. Richardson Bros. and Co.,
Manure Works, Belfast, January 22, 1896.

IS ARGON AS IDLE AS ITS NAME SUGGESTS.

To the Editor of the Chemical News.

SIR,—I should like to suggest to the authors of argon, Lord Rayleigh and Prof. W. Ramsay, who have all the appliances for its production, to ascertain whether the new gas has any action towards fermentation, either in retarding or facilitating it, and what effect has it in general.

Also what is the behaviour in the preservation of foods, such as milk, &c.

And its physiological action on bacteria.—Yours truly,
P. L. ASLANOGLU.

January 13th, 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxi., No. 27, December 30, 1895.

Acoustic Analysis of Mixtures of two Gases of different Densities.—E. Hardy.—The author attaches a microphone to each of two sonorous pipes. An electric current traverses them in succession, and then passes into an ordinary telephonic recipient placed at some distance. This recipient repeats distinctly either the pure sound or the beats produced by the sonorous pipes. With mixtures of air and coal-gas the author obtained:—For 1/1000th part of gas, 2 to 3 beats in twenty seconds; for 2/1000th part, about 6 beats in the same time; and for 20/1000th, 60 beats in the same time.

Spectral Displacement of the Solar Thermic Maximum.—M. Aymonnet.—The author gives his results in the form of tables, and concludes with the observation that the more crown glass is contained in the spectroscope the further the maximum is displaced towards the violet.

Combustion of Acetylene.—H. Le Chatelier.—Mixtures of acetylene with air containing a proportion of the gas below 7.74 per cent burn, yielding carbonic acid and water, with a yellowish flame feebly luminous. For proportions of acetylene between 7.74 and 17.37 per cent, the flame is of a pale blue with a slight yellowish halo. The products of the combustion are carbon dioxide, carbon monoxide, watery vapour, and hydrogen. If acetylene is burnt with an equal volume of oxygen it gives a temperature of 4000°; consequently superior by 1000° to the mixture of oxygen and hydrogen. The products of combustion consist exclusively of carbon monoxide and hydrogen, both reductive gases. This double property will render the use of acetylene in laboratories very valuable, either in the gas blowpipe for the production of high temperatures, or in ordinary air burners for spectrum analysis.

Fixation of Nitrogen by the Alkaline-earthly Metals.—L. Maquenne.—In the course of my researches on the alkaline-earthly metals, I have called attention to two novel and curious properties of these substances, *i.e.*, their power of forming directly definite compounds with carbon and nitrogen. I have thus obtained alkaline-earthly nitrides of the general formula NM₃. The barium compound has been obtained pure and crystallised. I am surprised that the power of these metals for the absorption of nitrogen has not been utilised in the preparation of argon.

Crystalline Titanium, and on the Compounds of Titanium and Silicon.—Lucien Lévy.—The author has obtained crystals of the following composition:—Ti, 76.14; Si, 22.69; various matters, 1.27. If we sup-

pose that the various matters are impurities, this would show a composition of Ti_2Si , i.e., 77.42 per cent titanium and 22.58 silicon.

Rotatory Property of Superfused Rhamnose (Isodulcite).—G. Gernez.—The rotatory power of superfused rhamnose decreases regularly as the temperature rises, and for a variation of temperature of 100° it becomes 61/100 of what it is at 0° .

Certain Dithioazolic Derivatives.—Charles Lauth. The author has formerly obtained methylene blue by causing sulphur to enter into the molecule of the colouring-matter. He has obtained two yellow substances, insoluble in water and ligroine, sparingly soluble in carbon disulphide and benzene, easily soluble in ether, acetone, and alcohol. The alcoholic solution of the base presents a splendid green fluorescence. Both the bases dye a fine yellow both on animal fibre and on unmordanted cotton. The colours resist acids and alkalis, but they are fugitive on exposure to light.

Synthesis of the Hydrochlorates of Amides and of the Chlorides of Acids.—Albert Colson.—The author mixes a nitrile with an acid and saturates the mixture, cooled down to 0° , with dry hydrochloric acid gas.

Action of the Halogens upon Formic Aldehyd.—A. Brochet.—The formation of carbon monoxide appears to be inherent in that of formic aldehyd by the oxidation of methylic alcohol.

Essence of Lemon Grass.—Ph. Barbier and L. Bouveault.—This paper is not suitable for useful abridgment, and is scarcely of sufficient importance for insertion in full.

Respective rôles of Philothion and Laccase in Seeds during Germination.—J. de Rey-Pailhade.—Laccase and philothion, possessing antagonistic chemical properties, meet simultaneously in many seeds capable of rapid growth, and the laccase destroys the philothion by oxidation. The two compounds occur simultaneously in beans, peas, white lupins, wheat, maize, and chestnuts.

Zeitschrift für Anorganische Chemie,
Vol. ix., Part 4.

New Phosphoric Acid, $H_5P_3O_{10}$. Some of its Compounds.—Fritz Schwarz.—Fleitmann and Hinneberg insert between pyrophosphoric and metaphosphoric acids two new compounds, the tetra- and tri-phosphoric acids; whilst decaphosphoric acid is as yet little known. The author describes here a number of tri-phosphates, i.e., those of cobalt, nickel, copper, barium, calcium, and zinc. The attempt to prepare the lead salt of tri-phosphoric acid yielded the tetraphosphate.

Determination of Fluorine by its Expulsion as Hydrofluoric Gas.—P. Jannasch and A. Röttgen.—This paper requires the two accompanying figures.

Separation of Metals in a Current of Hydrochloric Acid.—P. Jannasch and F. Schmidt.

Supposed Group of Inactive Elements.—Julius Thomsen.

Remarkable Change in the Structure of Glass by Heating.—E. Priwoznik.—Among the thin-sided tubes of soda-glass produced for chemical purposes, there are occasionally some which on heating undergo a strange modification of structure. At the temperature of boiling water the upper layer displays both within and without a vast number of fine cracks running in all directions. These cracks do not penetrate deeply into the glass, so that when the scales are rubbed off the body of the tube has not lost much in thickness.

On so-called Amido-chromates.—A. Werner and A. Klein.—The authors express surprise that Dr. S. Löwenthal can have closely examined the amido-chromates, effected transformations with them, and obtained correct analytical results without suspecting that he was simply working with bichromates.

Relations of the Colours of Atoms, Ions, and Molecules.—Carey Lea.—The commencement of this memoir, parts of a paper on the "Nitroso-compounds of Iron," and on some "Iodine Compounds of Lead with excess of Iodine," are wanting. As the main result of Carey Lea's article—which seems to be of profound interest—it is mentioned that: The colour of the elementary atoms is, broadly speaking, a function of the atomic weights. The atoms with atomic weights between:—1—47 are colourless; 52—59, coloured; 65—90, colourless; 103—106, coloured; 112—139, colourless; 145—169, coloured; 192—196, colourless. Elements which fall between these groups have both colourless and coloured atoms.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8. (Cantor Lectures). "Alternate Current Transformers," by Dr. J. A. Fleming, F.R.S.
Medical, 8.30.

TUESDAY, 28th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.
Society of Arts, 8. "Stamboul—Old and New," by Richard Davey.
Institute of Civil Engineers, 8.
Medical and Chirurgical, 8.30.
Photographic, 8.

WEDNESDAY, 29th.—Society of Arts, 8. "Standards of Light," by W. J. Diddin, F.C.S.
British Astronomical Association, 5.

THURSDAY, 30th.—Royal, 4.30.
Royal Society Club, 6.30.
Royal Institution, 3. "Dante," by Philip H. Wicksteed, M.A.

FRIDAY, 30th.—Royal Institution, 9. "National Biography," by Sidney Lee.

SATURDAY, Feb. 1st.—Royal Institution, 3. "Realism and Idealism in Musical Art," by Prof. C. Hubert H. Parry, D.C.L., &c.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1888.

PROFESSOR RÖNTGEN'S NEW DISCOVERY.

In the last volume of the *Transactions of the Würzburg Physico-Medical Society*, Professor Röntgen gives an account of his new discovery, which may doubtless prove to be of far-reaching importance in future.

If the discharges of a large Ruhmkorff tube are caused to pass through a Hittorf or a Crookes vacuum tube enclosed in black cardboard case, impervious to sunlight and electric light, as well as to ultra-violet rays, there appears, in a perfectly dark room, at each discharge, an illumination or fluorescence upon a screen coated with barium platino-cyanide. All substances are permeable for this newly-discovered agent, though in very different degrees. Thus the light was perceived behind a book of 1000 pages in thickness, as also behind boards of pine-wood of 2 to 3 c.m. in thickness, even on the introduction of discs of hard caoutchouc of several c.m. in thickness. Among the metals, aluminium was found to be permeable in a high degree, but lead and platinum are permeable only in very thin leaves. A sheet of tin-foil, laid between the apparatus and the screen, is scarcely perceptible. Salts, both solid and in solution, can be arranged in a similar series as regards permeability. Glass plates of equal thickness behave differently according as they contain lead or not; in the former case they are less permeable. Water and carbon disulphide have great permeability. The permeative power of this agent, which Röntgen names the "X rays," depends chiefly on the density of the material. But among metals it was observed that the permeability of different metals is by no means alike when they have the same thickness and density. Besides barium platino-cyanide, fluorescent phenomena are produced by the X rays with uranium glass, common glass, calc-spar, and the calcium compounds included among the phosphorescent bodies. The behaviour of the new rays with photographic plates is especially remarkable. By this use it is practicable to obtain proofs in a *camera lucida* in a closed case; or with plates wrapped up in paper. The photographs of different shadows are interesting; thus we may obtain the image of the bones of the hand by photographing the image of the hand. It is still questionable whether the chemical action upon the salts of silver proceeds directly from the X rays or from the fluorescent light arising in the glass plate, or in the layer of gelatin.

The retina of the eye is not sensitive to the new rays, even if we apply the eye close to the discharging apparatus. Experiments made with water and carbon disulphide in prisms of mica, and again with finely pulverised substances, showed that the X rays are scarcely, or not at all, refracted. Hence the rays cannot be concentrated with a lens. With the reflection of the rays the case is similar. The rays differ from Hittorf's kathode rays, especially by the fact that they are not deflected by the magnet. That part of the wall of the discharging apparatus which fluoresces most strongly must be regarded as the initial point of the X rays. Hence they proceed from the point on which the kathode rays impinge. If the kathode rays are deflected by a magnet within the apparatus, the X rays proceed from another point,—i.e., again from the terminal point of the kathode rays. If the X rays were violet or kathode rays, they must behave quite differently from the ultra-red, the visible, and the ultra-violet rays. Röntgen conjectures that the X rays may be due to longitudinal vibrations of the ether,

Professor Röntgen's X Rays.

In considering Röntgen's discovery, Prof. Boltzmann adheres to the view of the former, and extends his hypothesis, placing along with the three kinds of luminous rays (ultra-red, visible, and ultra-violet) the electric-light waves of Hertz, as transversal, but of greater wave-length. But he claims for the kathode rays and Röntgen's X rays a different nature. In the two latter he recognises longitudinal waves, which in the kathode rays are of extremely short wave-lengths, but of a greater wave-length in those of Röntgen. According to Boltzmann's view, the chief signification of Röntgen's discovery is that we are again made acquainted with a new agency. The discovery of Hertz's rays, and of the kathode rays, has occasioned a justifiable sensation. The former, however, are not essentially different from light waves, and the latter are almost exclusively confined in the narrow limits of the Hittorf tube, and are therefore sparingly accessible either for Science or for practice.

Röntgen's phenomenon is entirely new, and is displayed on a large scale.—*Chemiker Zeitung*.

ANALYSIS OF ALUMINIUM AND ITS ALLOYS.

By HENRI MOISSAN.

THE impurities which we encounter in commercial aluminium profoundly modify its properties, whence it is important to effect its analysis in the most accurate manner possible. The procedures hitherto employed in industry leave for the most part much to be desired, as when we regard as silicon the ferruginous residue which aluminium leaves on treatment with hydrochloric acid, or determine the aluminium as difference.

We have first to examine if the aluminium contains copper. We dissolve a small quantity of aluminium—about 2 grms.—in hydrochloric acid diluted with water, and treat the solution with a current of sulphuretted hydrogen. If the proportion of copper is very small it is useful to heat the solution gently, and to keep it at a hand heat for some hours after the passage of the sulphuretted hydrogen. We filter and search for the copper in the residue.

The qualitative analysis is then conducted so as to show the presence of silicon, iron, carbon, nitrogen, titanium, and sulphur.

1. Aluminium without Copper.

Determination of Silicon.—We weigh out about 3 grms. of the metal, which is then treated with pure hydrochloric acid diluted to one-tenth. If there remains a residue of a grey colour (containing silicon, iron, aluminium, and carbon) we separate this powder and attack it with a small quantity of melting sodium carbonate in a platinum crucible. The contents of the crucible are taken up in dilute hydrochloric acid, and this solution is added to the former. The liquid is put in a porcelain capsule and kept on the water bath until dry. The capsule is then placed in a hot air stove at the temperature of 125°. The residue should then be absolutely white, pulverulent, and should not adhere to the stirring rod. To obtain this result it is advisable to scrape the sides of the capsule with a spatula of platinum, and to crush any clots with an agate pestle. We remove the capsule after it has remained for 12 hours in the hot air stove, when it is observed that a stirring-rod moistened with ammonia and held above the residue no longer gives off dense white fumes, indicating that all escape of hydrochloric acid has ceased.

The desiccation being completed we take up the residue in luke-warm distilled water, to which has been added the smallest possible quantity of hydrochloric acid. The liquid is heated to ebullition for a few minutes, the silica remains insoluble and is thrown on a filter. After washing it is ignited and weighed. To be certain that this

silica does not contain alumina or ferric oxide we pour pure hydrochloric acid into the platinum crucible used in the last ignition. After evaporation to dryness in the sand bath no residue should be left.

Determination of Aluminium and Iron.—The original solution of the aluminium in dilute hydrochloric acid, after the separation of the silica, was diluted with water to the volume of 500 c.c. Of this solution we take 25 c.c., corresponding to 0.150 grm. of aluminium, neutralise it with ammonia in the cold, and precipitate the two oxides with recently prepared ammonium sulphide. The mixture is left to digest for an hour. The precipitate is then thrown upon a filter, washed, dried, ignited, and weighed.

We do not employ ammonia for this precipitation, for if it is to be complete the solution must not be too dilute, and must contain a sufficiency of ammonium salts and very little free ammonia. We may, indeed, get rid of the excess of ammonia by ebullition, but in this case we must stop when the liquid is only slightly alkaline, for if we exceed this point the alumina reacts slowly upon the ammoniacal salt, and the liquid takes an acid reaction. On account of these difficulties we prefer the precipitation with ammonium sulphide.

The precipitated alumina is very difficult to wash. It is necessary to effect the washing by decantation with boiling water in a cylindrical beaker of Bohemian glass. The washing is complete when the supernatant liquor no longer contains chlorine. The precipitate is then placed on a filter, dried, calcined, and weighed. We thus obtain the joint weight of the alumina and the ferric oxide contained in the aluminium. The iron is at first precipitated as a hydrated sulphide, but it is quickly oxidised by the washing and ignition.

It is very important to dry this alumina carefully before heating it to redness. The ignition must be effected slowly, because alumina if heated strongly sometimes decrepitates. Lastly, the ignition must be carried far enough, because alumina loses its water only under the action of a very high temperature.

Determination of the Iron.—To determine the iron we take 250 c.c. of the original solution after the separation of the silica. This liquid is reduced by evaporation to about 100 c.c. We add caustic potassa quite free from silica, which precipitates at first the iron and the alumina, and when in sufficient excess re-dissolves the latter.

The mixture is kept for ten minutes at a temperature close upon ebullition. The precipitate is washed by decantation five or six times with boiling water, and is then thrown upon a filter. It is re-dissolved in dilute hydrochloric acid and again precipitated with an excess of potassa. After washing and filtration it is again dissolved in hydrochloric acid, and this time the iron is precipitated with ammonia.

The precipitate is brought upon a filter, washed, ignited, and weighed. Proportionally we deduct from the weight of the two oxides obtained in the foregoing operations the weight of the ferric oxide, and the difference shows the weight of the alumina.

Determination of Sodium.—The method of determination is founded on the fact that the aluminium nitrate is destroyed by heat, yielding alumina at a temperature below that at which sodium nitrate is decomposed.

We take 5 grms. of aluminium—whether containing copper or not—in filings or in sheets; we treat them in a conical vessel with nitric acid diluted with an equal volume of water, applying a gentle heat. The action does not take place in the cold, but the temperature must be raised cautiously, as otherwise the disengagement of gas may be violent.

The solution is concentrated in a platinum capsule on the water bath, and then evaporated to dryness on the sand bath or over an open fire. The residue is brought to a pulverulent state by means of an agate pestle.

We heat then at a temperature which is below the fusion point of sodium nitrate until all escape of nitrous vapours has ceased. We then dissolve in boiling water,

decant the liquid, and wash the alumina three or four times.

At the same time we wash the pestle and the capsule, and all the washings, with the addition of a few drops of nitric acid, are evaporated to dryness. We dissolve three times in boiling water, each time eliminating a fresh quantity of alumina which has been mixed with the alkaline nitrate. Lastly, we treat with boiling water, evaporate in a porcelain capsule, add a slight excess of pure hydrochloric acid, and evaporate to dryness. We add a further quantity of hydrochloric acid, and after evaporation heat to 300° to expel any excess of acid. The sodium chloride remaining is determined as silver chloride. From the weight of the latter we deduct its quantity of chlorine, and calculate its equivalent weight of sodium.

Determination of Carbon.—We take 2 grms. of the metal in state of shavings or filings, triturate them in a mortar with from 10 to 15 grms. of mercuric chloride in powder, with the addition of a small quantity of water. The mixture is evaporated in a capsule on the water bath, and afterwards placed in a porcelain boat, which is then heated in a current of pure hydrogen. This boat is put into a tube of Bohemian glass and heated to redness. The gaseous current traverses a Liebig tube containing a solution of potassa and two small U-tubes filled with fragments of potassa. The increase of weight in these tubes gives in carbonic acid the quantity of carbon contained in the aluminium.

2. Analysis of Alloys of Copper and Aluminium.

When the alloy contains up to 6 per cent of copper we dissolve 0.5 grm. of the metal in nitric acid perfectly free from chlorine, we dilute the solution to the volume of 50 c.c. and effect the determination electrolytically. The current employed has an intensity of 0.1 ampère; the operation takes 6 hours at the temperature of 60°, or 24 hours in the cold. When the electrolysis is completed the copper is washed, dried, and weighed as metal.

Determination of Silicon, Aluminium, and Iron.—The author subjoins the analysis of a sample of aluminium from Pittsburg:—

Aluminium	98.82
Iron	0.27
Silicon	0.15
Copper	0.35
Sodium	0.10
Carbon	0.41
Nitrogen	traces
Titanium	traces
Sulphur	—
	100.00

A sample made at Neuhausen two years ago contained:—

Aluminium	96.12
Iron	1.08
Silicon	1.94
Carbon	0.30
	99.44

Along with the analytical results we must take into account mechanical data, extensibility, limit of elasticity, and breaking weight.—*Comptes Rendus*, cxxi., p. 851.

The "Pli Cachete" System.—The *Chemiker Zeitung* announces that it has opened a department for taking charge of sealed documents, containing a sketch of some incomplete scientific investigation which is not to be opened and made known except at the request of the author. This system has long been in use by scientific societies and journals in France. The object proposed is to furnish evidence in the case of dispute as to the priority of any discovery or invention. The system is, however, open to an abuse which we have pointed out on a former occasion.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 40.)

The Electric Spectrum of Lithium.—I wished to check my results by replacing the heat made by the burning oxy-hydrogen gas, by a spark from a small induction coil *without a condenser*, as M. Lecoq de Boisbaudran and M. Bunsen had already done when using chloride instead of oxide. For this purpose, after having carefully eliminated the sodium from the oxide of lithium, with an oxy-hydrogen blowpipe, and *whilst it was still heated up to the fusing-point of platinum*, I put into the liquid two balls of pure platinum, 3 m.m. diameter, attached to thick platinum wires, which had just been made white-hot and quickly cooled, so as to cover the balls with a fairly thick layer of oxide of lithium.

Having fixed the two balls at a convenient distance apart (from 2 to 3 m.m.), and in front of the Steinheil and Duboscq spectroscopes, I passed an induction spark between the two balls, by means of a small coil *without condenser*, and as strong as could be used without showing air lines: although the spark was *hardly* coloured purple, I recognised simply and solely the lines of the incandescent hydrogen flame spectrum, neither more nor less,—that is to say, *the sodium line was entirely absent*, but the three red, orange, and pale blue lines appeared. Notwithstanding that the number of lines in the electric and complete flame spectra of oxide of lithium is the same, there is yet a fundamental difference between the two spectra. In the flame spectrum the red line is very strong and brilliant, and the orange or yellow line is very weak, whilst in the electric spectrum it is the other way about—the red line is very weak, and the orange line is strong and brilliant. I saw no difference between the strength and colour intensity of the blue line in either spectrum. It is thus certain, as follows also from Bunsen's observations, that there is an essential difference between the *appearances* of the two lithium spectra. As for the *position* of the lines in the flame and electric spectra, I found them identical when taking *the solar spectrum as a standard of comparison for the two lithium spectra*.

Wishing to ascertain whether the spectrum of lithium would be changed by substituting a strong discharge for the spark from the small coil without a condenser, I replaced the small coil by a large Ruhmkorff coil with a condenser composed of *five* very large Leyden jars, taking care to adjust the solar spectrum previously as a standard of comparison.

Whether I allowed or stopped the passage of solar rays, I found the lithium spectrum identical, as regards the *number* and *position* of the lines, with that in the oxy-hydrogen blowpipe, with the addition, however, of some air lines; but at the same time I noticed an undoubted appearance, though extremely faint, of the sodium lines corresponding to the D and D₁ lines in the solar spectrum. When trying to account for the appearance of the sodium lines, I found that, on substituting pure platinum balls for those coated with oxide of lithium, spectrum analysis of a discharge showed the sodium lines in the *same* atmosphere, with the same degree of clearness as when passing through oxide of lithium. *I repeated this comparison several times, and always with the same result.* During this time, spectrum analysis of a Bunsen flame, burning in this same atmosphere, did not show a trace of the sodium line. Unfortunately, the contamination of the air by the presence and movement of the *three* people necessary for making observations, soon put an end to the experiments.

These investigations date from the month of December, 1878. I repeated them at different times, when the air was sufficiently pure, using in succession a spectroscope with one prism, and one with five prisms by M. Duboscq,

and I must say that I never worked in Brussels in indoor air, or even outer air, which was sufficiently free from sodium as not to give, during spectrum analysis of a *strong discharge*, unmistakable though faint signs of the presence of sodium, although it was absolutely impossible for me to see the sodium line in the same air with a Bunsen burner, or a spark from a small coil which did not show any air lines.

In this way are explained the facts mentioned above about platinum, silver, &c., which, when completely freed from sodium and then kept in air, attract this metal from it, and give, after a certain time, on spectrum analysis, absolute proofs of the presence of sodium. I call the appearance of the double D line an absolute proof. Thus also are confirmed the facts mentioned in the chapter "On the Nature and Amount of Soluble and Insoluble Mineral Matters in the Air of the Upper Part of Brussels," &c.

The possibility of ascertaining whether sodium be or be not present in the air, depends therefore on the amount of the metal in it, and on the method used to discover it.

I can see no other explanation of these phenomena. For instance, oxide of lithium, when freed from sodium by the method I have described, and left in air *sheltered from floating dust*, unmistakably shows the sodium line, after a time which varies according to the relative purity of the air; platinum balls coated with oxide of lithium act in the same manner. After being kept for several days under a bell-jar, they showed the sodium line in a spark from a small coil, just as though the oxide used had never been freed from sodium.

When checking my observations, in collaboration with M. Depaire, I had an opportunity for observing the same facts when using pure sulphate of lithium made by M. Bunsen. We then found that this sulphate, when heated on platinum balls, showed the sodium line faintly or not at all *in the same air*, according as it was used in a spark with or without a condenser, and that the coated balls, when left in air protected from dust, showed, with a spark *without a condenser*, on the next day, the sodium lines due to the sodium they absorbed from the air.

I have mentioned above that the spectrum of lithium in an electric discharge is identical with that in a weak spark. Since this paper was written Messrs. Liveing and Dewar have found a second blue line in the spectrum of lithium in an electric arc; we had therefore to re-examine the spectrum of lithium in the discharge, to ascertain whether there was, or was not, a difference between the lithium spectrum in a spark or discharge, and that in an electric arc.

It follows from the above facts that, under conditions where accurate experiments are possible without absorbing sodium from the surrounding medium, there is no connection between the characteristics given to flames by lithium in the form of oxide or sulphate, and that given by sodium compounds. Lithium and sodium are not convertible the one into the other; they behave like distinct bodies.

As for the spectrum of lithium, it is clear that the flame spectrum varies with the temperature in which the metallic compound is vaporised.

When using an analyser, of which the eyepiece, prisms, and lenses are of flint-glass, the spectrum of a weak or strong spark is identical with the complete flame spectrum (1879). The recent discovery by Messrs. Liveing and Dewar, of a second blue line in the lithium spectrum of an electric arc, renders new researches on the lithium spectrum in an electric discharge absolutely necessary.

When trying, with M. Depaire, whether it was possible, in the lithium spectrum in an electric discharge, to see the second blue line discovered by Messrs. Liveing and Dewar, using for the purpose, successively, a single prism spectroscope,—the same as that used by M. Lecoq de Boisbaudran in his researches,—then one of Messrs. Liveing and Dewar's direct vision spectroscopes, made by M. Hilger, our investigations were fruitless, whether we worked in

air and allowed for atmospheric lines, or caused the discharge after replacing the air by hydrogen.

In both cases we found, *beyond a doubt*, only a single blue line—that discovered by Messrs. Frankland and Lockyer. The result was quite different when substituting one of M. Hilger's spectroscopes with two half-prisms and eyepieces of *quartz*, for Duboscq's and the direct-vision spectroscope, both fitted with very refractive and absorbent flint-glass prisms. When using this fine instrument, we saw the second blue line, not only in the electric discharge, but even in a spark *without* a condenser, charged with lithium. The second line appeared, in this case, of a very pale blue tint.

The visibility or non-visibility of this second blue line in the spark or discharge spectrum, depends then entirely on the *analyser*. We have already mentioned that, when using M. Hilger's spectroscope with quartz prisms and lenses, we did not see the second blue lithium line in a flame spectrum (inner cone of lithium charged oxy-coal-gas). These facts being determined, it was hardly necessary to submit a lithium charged electric arc to spectrum analysis. Nevertheless, we undertook this research, for the purpose of satisfying ourselves as quickly as possible as to the influence of luminosity and of the analyser, and the permanence of the lithium spectrum.

With this object we made:—

- 1st. An electric arc by means of 33 Julien accumulator cells, giving at the terminals 10 ampères and 70 volts.
- 2nd. An electric arc by means of a gramme and Siemens's dynamo *coupled*, giving at the terminals 28 ampères and 70 volts.

In both cases, the electric arc passed between two pure carbon electrodes, consuming them without leaving a trace of ash; they were used in a Foucault lamp. The negative electrode, from 6 to 7 m.m. diameter, ended in a point; the positive electrode, about 12 m.m. diameter, ended in a flat surface, in which a small hole was drilled to receive the lithium compound to be volatilised in the arc.

As analysers, one of us used M. Hilger's spectroscope with two half-prisms and lenses of quartz, and the other Messrs. Liveing and Dewar's direct-vision spectroscope with flint-glass prisms.

After making the arc by putting the electrodes in contact, thus causing the fusion of the sulphate and chloride of lithium in the hole in the positive electrode, we saw, first with the current from the accumulator, then with the current from the *coupled* dynamos, the lithium spectrum, composed of its *four* lines (one dark red line, one orange-yellow line, the first pale blue line, and a second blue line paler than the first), appear, either on a very bright *continuous* spectrum, or on a *continuous* spectrum partially masked by the carbon spectrum of fine brilliant lines. These fine lines were as M. Fievez described them in his "*Recherches sur le Spectre de Carbone dans l'Arc Électrique*," and as Lieutenant-General Liagre and one of us had seen them whilst M. Fievez was carrying on his work at the Royal Observatory at Brussels.

In order that we might be able to carry on our observations for the time necessary to identify the lithium and carbon lines, an assistant was told off to introduce the lithium compound into the arc as it became volatilised, by means of a pure carbon rod. When the lithium compound was being introduced into the interior of the electric arc, it did not change colour, whilst the envelope was coloured deep red, especially towards the negative electrode. At the temperature of the electric arc, therefore, lithium vapour is blue, like the arc itself.

When working in this manner, we were able to demonstrate to certainty that the background of the spectrum consisted of a lithium spectrum on a continuous spectrum, or of a lithium spectrum on a continuous spectrum, masked by the fine lines caused by the resolution of the carbon bands, according as the electrodes *touched* or were *separated*,—that is to say, according as spectrum analysis

was made of the electrodes in contact but surrounded by lithium vapour, or of the arc containing vapours of carbon and lithium simultaneously. But in both positions of the electrodes, we saw the four lithium lines permanently, no more, no less.

One must therefore conclude that the spectrum of lithium, in an arc as powerful as we had at command, is permanent.

When using sulphate of lithium absolutely free from sodium, we did not see the double sodium lines in the spectrum; whilst when using chloride of lithium containing sodium, we found the double sodium lines in the spectrum.

(To be continued.)

ON THE OXIDATION OF SOME GASES WITH PALLADINISED COPPER OXIDE.*

By E. D. CAMPBELL.

(Continued from p. 33).

IN determining the rate of combustion of any gas the method was as follows:—The tube filled with air was carefully brought up to the temperature at which combustion was to be made, and maintained at this temperature until thoroughly heated through. A weighed calcium-chloride tube was attached to the outlet of the combustion-tube, followed by a double Liebig potash-bulb. The latter was made by uniting two ordinary Liebig bulbs and placing in the first bulb a solution of potassium hydroxide (1 : 2), and in the second bulb a stronger (1 : 1), the bulb being provided with the usual guard-tube. It was found necessary to have the potassium hydroxide in the first bulb more dilute than 1 : 1, since most of the carbon dioxide was taken up in the first small bulb, and if 1 : 1 potassium hydroxide was used potassium acid carbonate crystallises out so as to choke the tube. By using the more dilute solution in the first bulb the trouble is avoided. When the combustion-tube has attained the desired temperature, the pure gas under examination was forced through the tube, the rate at which it is supplied being so regulated that as light excess of unburned gas passes completely through the train. In the combustions shown in the table this excess of unburned gas was judged by the number of bubbles passing through the last small bulb of the potash bulbs, and the supply of gas was so regulated that this excess should come through at the rate of 6 to 10 bubbles per minute. The exact time at which the gas was introduced into the combustion-tube was noted. The gas at the commencement was introduced rather rapidly for a few moments to expel the air in the tube, then the flow regulated to the 6—10 in excess and kept up for times varying from 45 minutes to 6 hours, according to the rate at which the gas burned. At the end of an exact time, the stopcock was reversed and pure air drawn through the tube until all the products of combustion had been collected. From the weight of water and of carbon dioxide or of both obtained, the number of c.c. of pure gas required to produce these was calculated. In addition to the number of c.c. of each gas burned per hour has been calculated the weight of oxygen removed from the copper oxide for the combustion. In order to determine the extent to which palladium effected combustion, the ignition-point of the various gases was determined by passing the gas over a long plug of pure copper oxide made by oxidising pure copper gauze. This copper oxide was contained in a combustion-tube of the same size and heated in the same way as the one containing the palladinised copper oxide. It will be noted that the ignition-point of hydrogen has been reduced about 95°, that of

* Contributions from the Laboratory of Analytical Chemistry of the University of Michigan. From the *American Chemical Journal*, vol. xvii., No. 9, November, 1895.

ethylene 75°, of propylene 50°, of isobutylene 40°, while that of carbon monoxide, as would be expected, has not been affected.

In the preparation of gases the following methods were used :—

I. Hydrogen was prepared by the action of dilute sulphuric acid on pure zinc, and purified by passing through potassium hydroxide (1 : 1), over dry potassium hydroxide, calcium chloride, and phosphorus pentoxide.

II. Carbon monoxide was prepared by the action of strong sulphuric acid upon oxalic acid, the carbon dioxide being removed with potassium hydroxide, and the gas being then purified in the same way as the hydrogen.

III. Ethylene was prepared by the action of ethyl alcohol upon phosphorus pentoxide, and purified by passing through strong potassium hydroxide and then over three towers of dry potassium hydroxide. It was found in the course of the work that if phosphorus pentoxide was used in the train that there was some polymerisation with ethylene, and that this tendency to polymerise increases with propylene, and was so marked with isobutylene as entirely to prevent the use of phosphorus pentoxide. Ethylene produced from alcohol and sulphuric acid in the usual manner was found to contain so much carbon monoxide as to be unfit for this work, while that produced by the method used was shown by analysis to be practically pure.

IV. Propylene was prepared by carefully heating propyl alcohol and phosphorus pentoxide and purifying as in the case of ethylene. This method gives very nearly if not quite pure propylene.

V. Isobutylene was prepared by the action of isobutyl iodide upon alcoholic potash, the gas being collected over a 10 per cent solution of common salt, and then purified in the same way as ethylene and propylene. When an attempt was made to obtain isobutylene by the action of the corresponding alcohol upon phosphorus pentoxide, it was found the resulting gas contained only about 60 per cent of isobutylene and 35 per cent of butane.

VI. Methane was prepared by the action of methyl iodide on zinc-copper couple immersed in alcohol. It was purified by passing through strong sulphuric acid containing chromic acid and then through strong potassium hydroxide, followed by dry potassium hydroxide and phosphorus pentoxide.

VII. Acetylene was prepared by the action of calcium carbide on water. It was purified and dried by passing through strong potassium hydroxide and then over dry potassium hydroxide.

The details of the temperature and rate of combustion of the above gases, except ethylene, which does not oxidise perfectly to carbon dioxide and water, are shown in the following table. All rates of combustion have been calculated from the weight of water or carbon dioxide obtained to the c.c. of pure dry gas, under standard conditions, which would be burned in one hour. Since these combustions were all made in the same sized tube, and with practically the same amount of surface of copper oxide exposed, the rates of combustion are comparable. Of course varying the size of the combustion-tube, and with it the amount of palladised copper oxide present, would alter the absolute rates of combustion, but would probably not effect the relative rates.

(To be continued).

A SIMPLIFIED METHOD OF DETERMINING PHOSPHORIC ACID BY MEANS OF MOLYBDENUM SOLUTION.

By J. HANMANN.

THE author determines phosphoric acid by weighing directly the precipitate of ammonium phosphomolybdate. The method presupposes that no molybdic acid is sepa-

rated along with the ammonium phosphomolybdate. To prevent such a precipitation of molybdic acid we may precipitate a portion of the molybdic acid by previously repeated boiling from a molybdenum solution prepared according to Sonnenschein's formula, and then precipitate the phosphoric acid in heat with the molybdic solution over-charged with nitric acid. Or we may use a molybdic solution in the cold, which, after long and vigorous agitation of the mixed liquids, deposits all the phosphoric acid of the solution as a precipitate of constant composition.

As a matter of fact, it is possible to precipitate in the cold all the phosphoric acid, by vigorous agitation for half-an-hour with a solution of molybdenum containing to 100 grms. molybdic acid 1 litre of 10 per cent ammonia and 1½ litre nitric acid of sp. gr. 1·246, or with Maercker's solution, to which more ammonia has been added. The precipitate thus obtained, which is washed with a solution of ammonium nitrate, acidified with nitric acid, and dried, takes, on gentle ignition, a pure black-blue colour, and is constant in its composition, containing, in 100 parts by weight, 4·018 parts by weight of phosphoric acid. It is recommended to use the smooth compact filters of the firms Dreverhoff or Schleicher and Schull, as they allow of the precipitate being very completely removed from the paper, which is then burnt separately.

If the precipitate, after a gentle ignition, has not the proper blackish blue colour, it is moistened with a little ammonia, dried, and ignited again.

Organic matter is destroyed, before precipitation, by boiling with nitric or chromic acid. The ignition of the precipitate may be effected in a platinum crucible, or preferably on a net of platinum wire. The bottom of the crucible must not appear red-hot, though the wire net should. The method permits of the employment of very small quantities. The author has used it very successfully for superphosphates and arable soils.—*Chemiker Zeitung*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 19th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 46).

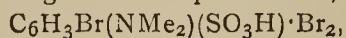
152. "*Researches on Tertiary Benzenoid Amines. I. Derivatives of Dimethylaniline.*" By CLARA DE BRERETON EVANS, B.Sc.

It is now established in the case of primary and secondary benzenoid amines, that the production of derivatives containing a substituent in the hydrocarbon nucleus is often preceded by that of the corresponding derivative in which the substituent is present in the amino-group; and inasmuch as compounds of the latter readily pass over into those of the former class, it is not improbable that their formation is a necessary step in that of many derivatives of benzenoid amines. As it is impossible, however, that similar derivatives should be formed from tertiary amines, the behaviour of these is of interest as throwing light on the influence which nitrogen itself exercises; and that this may be altogether different from that of nitrogen associated with hydrogen is clear from a comparison of benzenoid amines with *azophenes* (compare *Proc. Chem. Soc.*, 1892, 128) such as pyridine and quinoline, as these latter manifest a comparative indifference towards agents generally which is quite remarkable.

The experiments to be described have brought to light the fact that tertiary benzenoid amines manifest a somewhat similar indifference.

Dimethylaniline is readily sulphonated by means of chlorosulphonic acid, yielding only the *para*-acid; it is somewhat less readily, but yet easily sulphonated by means of a *single* molecular proportion of ordinary sulphuric acid, but if a larger proportion of acid be used, the action takes place less readily, sulphonation being incomplete at the end of *twelve hours* at 180° when five molecular proportions of acid are used, although it is complete within *five hours* when a single proportion is taken. Practically nothing but the *para*-acid is formed. To procure the *meta*-acid, it would seem that it is necessary to use fuming sulphuric acid—a point of some interest in connection with the moot question as to the manner in which isomeric sulphonic acids are generated. The behaviour of diethylaniline is similar to that of dimethylaniline.

The behaviour of the *para*-acid towards bromine is remarkable. It first yields a *monobromo*-acid. On adding bromine to a solution of this bromo-acid in muriatic acid, a crystalline orange-coloured perbromide,—



is precipitated. This is readily and simply deprived of its bromine by exposure to air, by boiling with water, and in contact with ammonia, sulphurous acid, or potassium iodide. If digested with muriatic acid on the water-bath in a closed vessel, it yields a small amount of tribromomethylaniline and some tetrabromodimethylaniline, together with much unchanged monobromo-acid; if digested with excess of bromine, it is entirely converted—but by no means easily—into tetrabromodimethylaniline. Under no condition, apparently, does it yield a dibromosulpho-acid or tribromodimethylaniline; in this respect its behaviour is most remarkable in comparison with that of ordinary sulphanilic acid, which is extremely sensitive to the action of bromine, being very readily converted into tribromaniline.

The *meta*-acid, in like manner, readily yields a *para*-bromo-acid identical with that obtained on sulphonating *para*bromodimethylaniline, and this is converted into a dibromo-acid by the further action of bromine. But all attempts to prepare a tribromo-acid corresponding to that which is so readily obtained from anilinemetasulphonic acid were unsuccessful. No perbromide is obtained from the *metabromo*-acids.

On nitration with nitric acid, dimethylanilineparasulphonic acid yields a mixture of orthoparadinitrodimethylaniline, together with orthonitroparasulphonic acid, the latter being the chief product. The *meta*-sulphonic acid yields a dinitrosulphonic acid. On warming a solution in dilute acetic acid of the orthonitroparasulphonic acid with bromine, a substance crystallising in red prisms, melting at 102°, is produced, which apparently is a bromonitromethylaniline.

The behaviour of the diethylanilinesulphonic acids is similar to those of dimethylaniline. The perbromide derived from the bromoparasulphonic acid is better characterised even than that derived from the dimethylated acid.

A full description of the various compounds referred to in this note will be given in a complete paper; it may be stated that all are exceedingly well-defined substances.

Experiments are in progress having for their object the comparison of the *ortho*-acids of dimethyl- and diethylaniline with the isomeric *meta*- and parasulphonic acids; and others are being made with the secondary amines to ascertain if their behaviour be, as is probable, similar to that of primary amines rather than intermediate between that of primary and tertiary. It is also proposed to largely extend these observations to other tertiary aminobenzenoid compounds, such as the dimethyltoluidines, dimethylamidophenol, and dimethylamidobenzoic acid.

For the supply of a large quantity of material used in these experiments, Dr. Armstrong is indebted to the Société pour l'Industrie Chimique à Bâle.

153. "*Experiments on the Formation of the so-called Ammonium Amalgam.*" By JAMES PROUDE and W. H. WOOD, F.I.C.

The fact, first clearly established by Wetherill, that sodium amalgam does not form the so-called ammonium amalgam when added to an aqueous solution of ammonia, enables sodium amalgam to be used as a test for the presence of ammonium salts, even in the presence of ammonia.

Solutions of phenol and of pyrogallol in aqueous ammonia were shown to contain compounds of the nature of ammonium salts; whilst sodium phosphate, calcium chloride, and magnesium sulphate, with aqueous ammonia, gave rise to no mercurial froth, showing absence of ammonium salts.

Ammonium sulphate, nitrate, and acetate when fused gave no mercurial froth on the addition of sodium amalgam. Ammonium chloride, oxalate, acetate, benzoate, tartrate, and succinate, dissolved in absolute alcohol, rectified spirit, and methylated spirit, in no case gave a definite mercurial froth with the sodium amalgam, either cold or hot, though the acetate and benzoate dissolved in rectified spirit, and the chloride in methylated spirit, showed indications of swelling of the mercury. Water, therefore, appears to be necessary to the production of a definite froth.

The sp. gr. of the well-formed mercurial froth is not higher than 0.730, since it floats in methylated ether of that density.

154. "*The Molecular Volumes of Organic Substances in Solution.*" By W. W. J. NICOL, M.A., D.Sc.

In 1883, and again in 1892, the author directed attention to the probability that a study of the molecular volumes of organic substances in solution would lead to results from which the atomic volumes of the various elements could be determined with an ease and accuracy impossible by Kopp's method of determining the volume at the boiling-point.

The paper contains an account of determinations made on fourteen esters in dilute solution in various solvents. The chief conclusions drawn are as follows:—

1. The volumes of isomeric esters are approximately the same.
2. The volume of CH_2 is a constant for each solvent, being 16.8 in xylene, 17.0 in benzene, 17.3 in 88 per cent alcohol, except
3. In the case of ethyl oxalate and succinate, where the value is about a unit less, owing probably to contraction resulting from the separation of the two carboxyl groups.
4. The nature of the solvent has a marked effect on the molecular volume, which is less in the solvent with the higher molecular weight.

155. "*2 : 1 β -Naphthylaminesulphonic Acid and the corresponding Chloronaphthalenesulphonic Acid.*" By HENRY E. ARMSTRONG and W. P. WYNNE.

Tobias has recently shown (Germ. Pat. 74,688, February 19, 1893) that the acid obtained by one of us (Armstrong, *Ber.*, xv., 1882, 202) by the action of chlorosulphonic acid on β -naphthol at the ordinary temperature is not β -naphthylsulphuric acid, $\text{C}_{10}\text{H}_7\cdot\text{O}\cdot\text{SO}_3\text{H}$, but the isomeric 2 : 1- β -naphtholsulphonic acid, and in the same patent has described the amido-acid obtained by heating the hydroxy acid with strong aqueous ammonia under pressure at 220–230°. Being desirous of examining the amido-acid, the authors applied to Dr. Tobias for a sample, and he not only sent them a carefully purified specimen of the sodium salt of the β -naphthylaminesulphonic acid, but courteously forwarded their letter to the Farbwerke vorm. Meister, Lucius, and Brüning, who, with characteristic liberality, furnished them with a considerable quantity of the technical product. After purification, the acid was found to have all the characters described in the patent; its sodium salt, as there stated, crystallises from dilute alcohol in monohydrated scales.

The acid was converted by the Sandmeyer method into the corresponding 2 : 1- β -chloronaphthalenesulphonic acid, which has not hitherto been described, and is the twelfth of the fourteen isomerides which it is theoretically

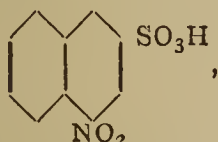
possible to isolate. This acid yields an easily soluble mono-hydrated microcrystalline *barium* salt, a mono-hydrated *potassium* salt crystallising in thin scales, and a monohydrated *sodium* salt crystallising in long slender needles. The *chloride*, $\text{Cl} \cdot \text{C}_{10}\text{H}_6 \cdot \text{SO}_2\text{Cl}$, crystallises from a mixture of benzene and light petroleum in large tabular forms, and from acetic acid in diamond-shaped scales melting at 76° ; it yields an *amide* crystallising in slender needles melting at 153° , and on distillation with phosphorus pentachloride is converted into 1 : 2-dichloronaphthalene, melting at 35° .

On sulphonation with four times its weight of cold 20 per cent anhydrosulphuric acid, the 2 : 1- β -naphthylaminesulphonic acid is converted into the 2 : 1 : 4'- β -naphthylaminedisulphonic acid, previously described by the authors as the minor product of sulphonation of the Dahl 2 : 4'- β -naphthylaminesulphonic acid under similar conditions (*Proc. Chem. Soc.*, 1890, 129).

The investigation of the 2 : 1- β -naphthylaminesulphonic acid and its derivatives is being continued.

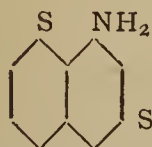
156. "1 : 3- α -Naphthylaminesulphonic Acid and the corresponding Chloronaphthalenesulphonic Acid." By HENRY E. ARMSTRONG and W. P. WYNNE.

In the course of their study of the formation of isomeric naphthylene derivatives, the authors had occasion to attempt the repetition of Clève's work on the nitration of naphthalene- β -sulphonic acid, since of the three acids obtained by him in this way, one was stated to have the constitution—



the other two being the isomeric heteronuclear α -nitroacids. Whilst successful in obtaining two heteronuclear acids, of which they determined the constitution, they were unable to prepare the homonuclear compound by the nitration of potassium naphthalene- β -sulphonate (*Proc. Chem. Soc.*, 1889, 17). Particular interest attached to the question whether this acid was formed, inasmuch as—to repeat the words used at the time—"it has always been found that a heteronuclear α -derivative is formed in cases in which the corresponding benzene derivative would afford a meta-derivative." Although thus unsuccessful, they were, as they then said, "loth to accept the apparently logical interpretation of their results, as they were unacquainted with the precise conditions under which Clève worked . . . and as it is within their own experience that slight variations in treatment, such as may escape notice, may materially affect the result," and expressed the hope that Clève would supply further details as to the procedure adopted by him. Subsequently it came to their knowledge that the homonuclear acid also could not be detected in the product obtained on nitrating sodium naphthalene- β -sulphonate on the large scale. Moreover, Erdmann and Süvern have failed to obtain the corresponding chloride by nitrating naphthalene- β -sulphonic chloride (*Annalen*, cclxxv., 252).

It is particularly instructive, therefore, to record the fact that the so-called [γ] naphthylaminesulphonic acid which Clève prepared by reducing the homonuclear nitroacid he obtained by nitrating sodium naphthalene- β -sulphonate (*Ber.*, xix., 2179; xxi., 3271) is identical with the 1 : 3- α -naphthylaminesulphonic acid of Kalle and Co.'s German Patent 64979, prepared from α -naphthylamine-[ϵ]-disulphonic acid—which the authors have shown has the constitution—



(*Proc. Chem. Soc.*, 1890, 15)—by partially hydrolysing it with diluted sulphuric acid, and which, as Friedländer

has recently shown, may also be obtained by partially reducing the said disulphonic acid with sodium amalgam (*Ber.*, xxviii., 1951).

Through the kind offices of Dr. Hepp, the authors are much indebted to Messrs. Kalle and Co. for a supply of this acid in the pure form; the experiments they have made with it confirm Clève's statements as to the properties of this acid and the derived 1 : 3- α -chloronaphthalenesulphonic acid in every particular. There is nothing to add to the description of the salts of the amido- and chloro-acids as given in Clève's later paper, but the authors have been able to carry the identification of the acids a stage further, since they find that the dichloronaphthalene, melting at 61.5° —obtained from the chloronaphthalenesulphonic chloride melting at 106° —on sulphonation gives products characteristic of 1 : 3-dichloronaphthalene (*Proc. Chem. Soc.*, 1890, 82) and not of the 1 : 2'-isomeride of about the same melting-point with which it was for a while confused.

157. "Studies on the Constitution of Tri-derivatives of Naphthalene, No. 15. The Disulphonic Acids obtained by Sulphonating 1 : 3- α -Naphthylamine- and 1 : 3- α -Chloronaphthalene-sulphonic Acids." By HENRY E. ARMSTRONG and W. P. WYNNE.

As already announced (*Proc. Chem. Soc.*, 1890, 18, 131, 133; *Brit. Assoc. Report*, 1893, 382, footnote), the authors are engaged on experiments having for their object the determination of the comparative influence exercised by the radicles Cl, OH, and NH_2 , in naphthalene derivatives on the formation of disulphonic acids. Certain results arrived at in the case of β -derivatives have already been communicated (*Proc. Chem. Soc.*, 1890, 128, *et seq.*), but progress with the work was retarded so long as the characteristics of the reference compounds—the trichloronaphthalenes—were in doubt. The fourteen theoretically possible isomerides being now known and characterised (*Proc. Chem. Soc.*, 1895, 84), the authors hope shortly to complete their investigation of the products obtained on sulphonating the known naphthylamine- and chloronaphthalene-sulphonic acids. In the meanwhile, in view of the interest attaching to the 1 : 3- α -naphthylamine-sulphonic acid, they think it well to put on record the results obtained on sulphonating it and the corresponding chloro-acid, so far as their experiments have gone.

When dry 1 : 3- α -naphthylaminesulphonic acid is stirred into four times its weight of 20 per cent anhydrosulphuric acid at a temperature not exceeding 20° , it is converted in the course of 12 hours into what appears to be a single disulphonic acid. The normal potassium salt being very soluble, the acid was isolated in the form of the dihydrated acid *potassium* salt, which crystallised in radiate groups of short brittle needles. On reduction by the hydrazine method it gave naphthalene-1 : 2'-disulphonic acid (*Proc. Chem. Soc.*, 1890, 126) since the *chloride* obtained from it crystallised from acetic acid in glistening scales, melting at 122° , convertible by phosphorus pentachloride into 1 : 2'-dichloronaphthalene melting at 65.3° , and giving on sulphonation the characteristic chloride melting at 117° when opaque (*Proc. Chem. Soc.*, 1890, 83). By the Sandmeyer process, it was converted into a chloronaphthalenedisulphonic acid, the *chloride* of which, $\text{Cl} \cdot \text{C}_{10}\text{H}_5(\text{SO}_2\text{Cl})_2$, crystallised from a mixture of benzene and light petroleum in radiate groups of prismatic needles, and from acetic acid in small prisms, melting at 130° , which on distillation with phosphorus pentachloride gave 1 : 3 : 4'-trichloronaphthalene crystallising from alcohol in long slender flat needles melting at 103° .

When dry potassium 1 : 3- α -chloronaphthalenesulphonate is sulphonated under the conditions described in a previous note (*Proc. Chem. Soc.*, 1890, 131) by adding it to the theoretical quantity of sulphuric anhydride used in the form of 20 per cent anhydrosulphuric acid, and heating the warm mixture at 100° for an hour, it is converted into a *chloronaphthalenedisulphonic acid* identical with

that just described. No trace of an isomeric acid was detected. As in previous cases, details as to the composition of the salts, &c., are reserved for the complete paper.

It follows, therefore, that under the conditions described the disulphonic acids obtained both from the 1:3- α -amido- and the 1:3- α -chloro-monosulphonic acids have a corresponding constitution expressed by the symbols—



PHYSICAL SOCIETY.

Ordinary Meeting, January 24th, 1896.

Captain W. DE W. ABNEY, President, in the Chair.

MR. CAMPBELL SWINTON exhibited some Photographs which had been taken by Prof. Röntgen's method.

These included several of metal objects inside wooden and cardboard boxes, and a very clear and sharp photograph of the bones of the hand.

Mr. E. SCOTT showed some Geometrical Instruments invented by himself and Signor Monticolo.

The instrument designed by Signor Monticolo is intended for drawing arcs of circles of such large radius that compasses cannot be employed. It can be used to trace arcs of circles of which the radii vary from 50 c.m. to infinity.

The second instrument exhibited was a modified form of hatchet planimeter which Mr. Scott has devised with a view of avoiding some of the defects of the ordinary form of instrument. Thus, to avoid the cutting of the paper, which occurs when the knife edge is sharp, and the side-slip which occurs when the knife edge is blunt, the author uses a wheel with a sharp edge. To avoid the inclination of the instrument to one side, which may easily occur with the ordinary form, a flat celluloid plate with a dot at the centre is used as the tracing point; this plate being kept pressed flat on the surface of the paper. A small wheel with a recording disc is attached, and may be used to measure the distance between the first and last position of the knife edge.

Mr. Scott also described a form of planimeter which he had invented, and in which the disc and cylinder movement is used to perform the integration.

Mr. C. V. BOYS said that an instrument designed by Mr. Clarkson had been exhibited before the Royal Society which was capable of drawing arcs of circles of large radius. This instrument only drew an approximation to a circle, but the approximation was so close that it nowhere was more than the thickness of a thin ink line away from the truth. It would be interesting to hear from the author whether Signor Monticolo's instrument drew a rigorously exact circle or not. The upright position of the hatchet planimeter might be secured by using two wheels in place of one. The planimeter described was really a modified form of one he (Mr. Boys) had described before the Society in 1881.

Mr. BLAKESLEY gave a short geometrical proof showing that the curve traced by Signor Monticolo's instrument was rigorously an arc of a circle. Mr. Blakesley also drew attention to the fact that the instrument in its present form cannot be used to trace the arc on both sides of the zero line.

Dr. C. V. BURTON described an idea for an instrument for drawing circular arcs which had occurred to him, depending on the use of two wheels of different radii connected by an axle conveying a tracing point.

In the absence of the author, a paper by Prof. J. D.

EVERETT, on "Resultant Tones," was read by Dr. C. V. BURTON.

The author, after giving a short summary of the Helmholtz theory of the production of resultant tones, goes on to discuss his objections to this theory, and to elaborate a theory of his own. This theory depends on the consideration that if you analyse into a Fourier series a periodic curve which is compounded of two simple harmonic motions, of frequencies n and m , then only two terms are obtained. If, however, some error has been originally made in adding the two simple harmonic motions together, this error being repeated for each wave, then, in addition to the two terms of frequency n and m , there will be obtained, when the curve is analysed, a term of frequency f ; where f is the greatest common measure of n and m . This term of frequency f the author calls the common fundamental of the tones n and m . The "error" in the production of the compound curve, the author supposes to be produced during the transmission of the sound by the ossicles of the ear. In support of his theory the author finds that in the violin, where the sound-post, like the ossicles of the ear, transmits the vibrations from one portion of the instrument to another, it is easy by sounding two strings in conjunction to obtain combination tones which agree in frequency with those required by this theory. Thus, when the major sixth (3:5), the major second (8:9), or the minor seventh (5:9) are sounded, the fundamental (1) is clearly heard, and also felt by the hand holding the instrument. The author has also succeeded in picking out and strengthening this resultant tone by holding a Helmholtz resonator in contact with the body of the violin.

Dr. C. V. BURTON, after explaining several portions of Prof. Everett's paper, said that he (Dr. Burton) considered that the author's view in many ways seemed to fit in with the observed facts better than the accepted theory, but still did not appear itself quite free from objection. Prof. Everett supposes that the first term in a Fourier series is always the most important, and although in most cases which occur in practice this may be so, it hardly seems legitimate to take this as a characteristic of a Fourier series.

The thanks of the Society having been given to Prof. Everett and Dr. Burton, the meeting adjourned to February 14th.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Fourth Ordinary Meeting, January 13th, 1896.

Dr. J. E. MACKENZIE in the Chair.

Mr. KERR read a paper on "The Paraffin Industry."

He mentioned that the industry is a comparatively modern one, and was founded by the late Dr. James Young, of Kelly. The Boghead mineral, originally used, was exhausted in 1862, and since that time the main source has been the bituminous shale lying under the coal formations. About two million tons of this mineral are mined annually in this country.

The lecturer went on to give a description of the process as carried out in the works of the Linlithgow Oil Co., Lim., near Linlithgow, to which there was an excursion of the Society during the summer.

In these works about 700 men are employed, of whom fully one-half are miners.

On an average, 550 tons of shale are brought to the surface each day.

From the mine-head, after being disintegrated in the "breaker," the shale is conveyed in hutches to the top of the retorts, into which it is tipped.

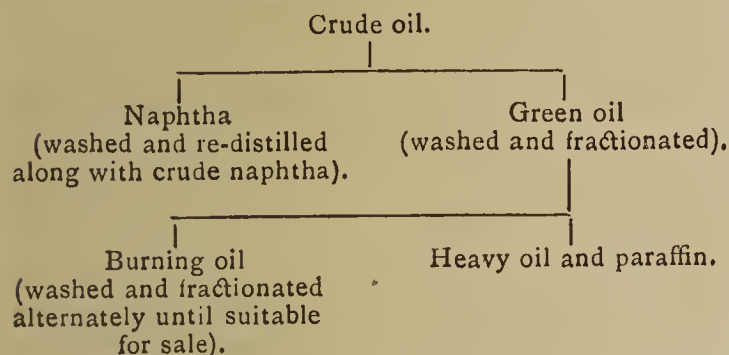
The retorts in use in the Linlithgow works are of the Young and Beilby type, having a re-distillation chamber in connection with each set of four. The coal-furnaces

are of brick-work, and are placed between the sets of retorts, two of them serving to heat eight shale retorts. Round these latter are the flues in which the gases from the furnaces are consumed.

From the shale are obtained directly:—The crude oil, ammonia water, and gases containing volatile hydrocarbons.

The crude oil yield depends on the form of retort and nature of the shale used, varying from 17 to 35 gallons per ton of shale. The ammoniacal liquor yields from 17 to 80 lbs. of ammonium sulphate, and the retort gases, when scrubbed, about $1\frac{1}{2}$ gallons of naphtha per ton of shale.

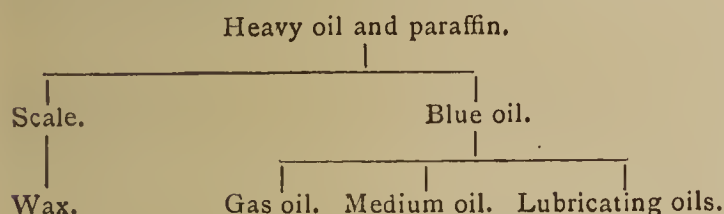
After being settled and separated from the ammonia liquor, the crude oil is put through a series of washings with acid and soda and fractional distillations.



The burning oils vary in gravity from 0.800 to 0.820. The flash-point in Scotch oils is never below 100° F., rarely below 110° F., while a large quantity of oil is imported from America flashing at or even below 73° F.

The heavy oil and paraffin is frozen and pressed. Solid paraffin (known as "scale" when in the crude state) is left in the filter presses, while blue oil passes through.

This latter undergoes further treatment with acid and soda, and is fractionated into gas and lubricating oils.



The lubricating oils are displacing vegetable ones for machinery, since they neither clog nor are liable to spontaneous combustion.

The paraffin scale, after further pressing, is purified by "sweating" out the oil and colouring-matters, and is then washed with bone-black, filtered, and run into cakes.

The lecturer then described the method of candle manufacture in some detail.

The paper was illustrated by diagrams and specimens of the products in various stages.

In the discussion which followed, the Chairman, and Messrs. Watson, Fairbairn, Smith, Lauder, and Gregory took part.

Mr. CLARKSON pointed out that when stearine is added to the wax in candle making, although the wax is rendered harder, the melting-point is lowered.

The meeting concluded with the usual votes of thanks.

The State of Sulphur in the Products of the Combustion of Coal-Gas.—In a series of experiments the proportion of sulphur in the products converted directly into sulphurous anhydride was found to be respectively 93, 89, 99, and 93 per cent of the total sulphur. Hence the authorities who maintain the direct formation of sulphuric acid are in error.—*Revue Universelle des Mines et de la Metallurgie*, xxxi., No. 1.

NOTICES OF BOOKS.

Notes on the Nebular Theory in Relation to Stellar, Solar, Planetary, Cometary, and Geological Phenomena. By WILLIAM FORD STANLEY, F.R.A.S., F.G.S., F.R. Met. Soc., M. Phys. Soc. London: Kegan Paul, Trench, Trübner, and Co. (Ltd.). 1895. 8vo., pp. 259.

FROM a first glance at the title of this work we were led to expect a discussion of the origin of the elements, and indeed of matter in general. As such researches, despite the protests of Positivism, have an intense fascination for minds who do not despair of the progress of Science, we opened it eagerly; but we at once found that there is here little to claim the attention of the chemist as such. Mr. Stanley has revised the celebrated nebular theory of Laplace, applying it to the sizes, the respective distances, and the temperature of the planets,—to the configuration of the earth's surface, to the glacial epoch, and other astronomical and geological phenomena. We find, indeed, that he accepts the concept of a *protyle*, and suggests the possibility of a number of elements much exceeding those which have been respectively isolated. The dissociation units, or *pneumites* as he terms them, must, he considers, be very much smaller than the atom, probably not exceeding $1/10,000$ th of its diameter. He thinks that atoms formed of pneumites of perfectly concordant period will be stable, such as gold. Atoms formed of pneumites partly of slightly discordant period will be unstable. Atoms may have concordant periods of vibration, though their pneumite composition may be partially discordant with other atoms. Matter formed of such concordant atoms with other atoms would have a tendency to associate in chemical combination or alloy, as nickel and cobalt, the two groups of the platinum metals, yttrium and didymium, &c. Here the author refers to the well-known address of Mr. Crookes to the Chemical Society in 1888.

Mr. Stanley, as we are not sorry to find, is unable to accept the brachychronology of Lord Kelvin, or the hypothesis of an earth solid and rigid to the centre. Nor does he admit of uniformly progressive cooling of the sun—a point of great weight in speculations on the cause of glacial epoch; but he has no doubt concerning the ultimate dismal fate of our planet, and the death of the "last man," from cold and hunger, in what is now the deepest part of the bed of the Pacific.

To astronomers and geologists the work will be suggestive reading.

Machinery and Appliances for Manufacturing Chemists. By JAMES C. SHEARS, Assoc. Inst. C.E. London: E. Marlborough and Co. 1895. 8vo., pp. 93.

THE selection and construction of apparatus for the various branches of manufacturing chemistry is now a matter of great importance, as a process which gives excellent results in the laboratory may, on a commercial scale, prove utterly useless for want of suitable mechanism. Hence the little work before us may be in many cases of great utility.

The general remarks on chemical factories speak of practical experience. Concerning the water-supply of such establishments, it may be added that its quality is of capital moment. The more closely it approaches distilled water the better. Hard waters, and such as contain iron, should on no account be used.

The author gives a comparative table of the value of different fuels, Welsh coal being taken as unity.

The subject of distillation has its painful side. According to the letter of the law, every apparatus for this purpose is still subject to an excise impost, however incapable it may be of serving for the manufacture of alcohol. Hence the exemption which chemists now practically enjoy is merely of courtesy, and not of right.

We regret to find that Mr. Shears has omitted auto-claves, which are indispensable for the production of coal-tar colours, and monte-jus. Perhaps, in the very probable case of a second edition being called for, he will introduce these subjects, and also the electric furnace, which is now doing such good service.

Bleaching and Calico Printing: a Practical Manual. By GEORGE DUERR, Director of the Bleaching, Dyeing, and Printing Department at the Accrington and Bacup Technical Schools, Chemist and Colourist of the Irwell Print-Works. Assisted by WILLIAM TURNBULL, of Turnbull and Stockdale (Ltd.). With Diagrams of upwards of 100 Dyed and Printed Patterns, designed to show various stages in the processes described. London: Griffin and Co. (Ltd.). 1896. 8vo., pp. 142.

THIS work, as the reader will perceive, does not extend to the bleaching and printing of tissues in general, but exclusively to cotton goods. Hence the list of mordants is reduced as compared with those necessary thirty or forty years ago. The extent to which coal-tar colours have superseded the natural dyes and pigments has acted in the same direction. The author admits that for general bleaching purposes nothing has yet been discovered preferable to the hypochlorites, some of which are from time to time advertised, under new names, as novel inventions.

We see that in the dunging process no arseniates are recommended—a step in the right direction. The same remark applies to the extract styles, in which arsenical and antimonial ingredients are no longer recommended, though they admit of beautiful effects being produced with the basic colouring-matters. We are glad to find the admission that artificial indigo is still not much used. It is a remarkable and unpleasant fact that for a "chrome yellow" that prepared by Bayer and Co. is directed to be used. Can we not make a satisfactory chrome yellow in Britain? The same applies to "brilliant yellow,"—i. e., cadmium sulphide. If, after all the labours of the syllabus constructors, we cannot produce such simple colours at home, something is in need of alteration.

The part taken by Read, Holliday, and Sons, in the production of diazo colours directly upon the tissue, is duly recognised.

Blood-albumen has of late been so much improved that egg-albumen is rarely used as a thickener, thus greatly cutting off a waste of human food.

In the removal of grit from colours prepared for printing there is still room for invention.

We question whether any of the coal-tar colours can be pronounced more brilliant than safflower and its extract carthamine.

The demands made on soaps by the printer and dyer are fully explained and justified.

The theory of colours is considered at some length. The author or authors (?) do not accept the modern theory of three primitive colours,—red, green, and violet,—but consider that they are practically three others, red, yellow, and blue.

Guide to the Determination of Molecular Weight according to Beckmann's Freezing- and Boiling-points Methods. (Anleitung zur Molekular gewichts bestimmung nach der Beckmannschen Gefrier- und Siedpunkts Methode).

THE author explains and illustrates Prof. Beckmann's two methods of ascertaining the molecular weights of substances by means of the freezing-point and the point of ebullition. He appends the caution that, in the former method, abnormal values may be produced by the joint crystallisation of the dissolved substance. In the ebullition method errors may occur if the substance is volatile, i. e., if its point of ebullition is not at least 150° higher than that of the solvent.

CORRESPONDENCE.

ACETIC ACID DISTILLATION.

To the Editor of the Chemical News.

SIR,—I shall feel obliged to any of my confrères experienced in acetic acid distillation from the commercial brown acetate of calcium, calculated as 68 per cent of acetate, distilled with hydrochloric acid of about sp. gr. 1.1599 (32.213 per cent), if they would give me commercially the yields of real acetic acid.

I wish to know the above through the chemical public with a view to some discussion.—I am, &c.,

P. L. ASLANOGLU.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 1, January 6, 1896.

M. Marey, the retiring President, gave the usual yearly notice of the condition of the Academy, the death of members and foreign associates during the past year, and the election of new members in their place.

The death-list includes Pasteur, Verneuil, and Larry. The academicians elected are Hautefeuille, Guignard, Lannelongue, and Carnot.

Two members have still to be elected; one for the section of Mineralogy, and one as a "free Academician." The foreign associates elected are:—Weierstrass, of Berlin; Frankland, of London; and Newcomb, of Washington.

Among the deceased correspondents we notice that Professor Huxley is described as "of Odessa." Prof. van Beneden is spoken of as deceased, and also as advanced from the rank of a correspondent to that of a foreign associate.

In the section of Anatomy and Zoology anti-evolutionism seems still predominant.

The Perpetual Secretary announced the death of J. Russell Hind, and F. Tisserand gave an account of the work of the late astronomer.

Action of Nitrogen Peroxide upon the Haloid Salts of Tin.—V. Thomas.—The author refers to the previous researches of Kullmann, Weber, and Hampe, on the action of the nitrogen oxides on the haloid salts of tin. He has resumed the study in a chloroformic solution of the compounds which are formed by the action of NO₂ upon all the haloid persalts of tin. With SrCl₄ the reaction is very brisk, producing a crystalline precipitate of the composition SnOCl₂ SSnCl₄.N₂O₅. It is soluble in water, hygrometric, and if heated it is decomposed, yielding a crystalline sublimate. The action upon SnBr₄ yields a white powder, partially soluble in water with decomposition. On heating it is decomposed into stannic acid and nitrous vapour, with probably nitrogen oxybromide. The residue is stannic acid. With SnI₄ the reaction is more difficult. There is produced a voluminous precipitate of iodine. The white product, when free from iodine, is not crystalline and insoluble in water, by which it is not affected.

On a Method of the Decomposition of some Compounds having an Amide or a Bromide Function.—Oechsner de Coninck.—The author has submitted several aromatic derivatives to the action of Leconte's reagent. See *Comptes Rendus* (1895; Dec., 1896).

No. 2, January 13, 1896.

At the meeting of the Society, January 13th, Marcel Bertrand was elected a member of the Mineralogical Section, *vice* Pasteur, deceased.

A Photometric Standard with Acetylene.—J. Violle.—Acetylene, in the author's model, issues from a small conical orifice carrying with it the necessary quantity of air. It then penetrates, by a narrow aperture, into a tube where the mixture is effected, and which terminates with a bat's-wing burner made of steatite. The entire flame corresponds to more than 100 candles under the pressure of 0.30 metre of water. The consumption of ethylene is 58 litres per hour. We see that the illuminating power of acetylene is more than 20 times that of coal-gas burning in a Bengel burner (giving 1 carcel = 9.6 candles for 105 litres), and at least 6 times that of the same coal-gas for an Auer burner (giving 1 carcel for 30 litres).

Formation-Heat of some Compounds of Manganese.—H. Le Chatelier.—Metallic manganese evolves a rise of temperature of 164 cal. Manganese carbide yields 5.2 cal. Manganese protoxide evolves 45.4 cal. Manganese dioxide gives 63 cal. Manganese carbonate 13.8 cal. Manganese silicate 2.7 cal.

Crystalline Strontium and Calcium Iodides.—M. Tassilly.—A thermochemical paper, the chief novelty of which is an apparatus for drying the substances in a current of dry air deprived of carbonic acid.

On the Aldehyds Derivatives of the Isomeric Alcohols, $C_{10}H_{18}O$.—Ph. Barbier and L. Bouveault.

On the Multirotation of the Reductive Sugars and of Isodulcite.—M. Tanret.—These two papers are not suitable for useful abstraction.

Journal für Praktische Chemie.
New Series, Nos. 8 and 9, 1895.

Communications from the Chemical Institute of the University of Kiel. Hydrazides and Azides of Organic Acids. Treatise V. — 27. On Substituted Glycolic Esters and Glycol Hydrazid.—Th. Curtius. — The author, with the co-operation of M. Schwann, examines here the substituted glycolic esters from diazoacetic ester; that is, 1, glycolic ester; 2, phenylglycolic ester; 3, benzylglycolic ester; 4, ethylglycolic ester; 5, benzoylglycolic ester; 6, hippuryglycolic ester; 7, oxalyglycolic ethyl ester; 8, succinylglycolic ester; the action of hydrazinhydrate upon the substituted glycolic esters—that is, that of hippurylglycolic ester, oxalyglycolic ester, succinylglycolic ester, and benzylglycolic ester. The authors next examine glycolhydrazid, its fission in acid solution, its compounds with aldehyds and keto-substances, such as benzalglycolylhydrazin and its ortho- and para-modifications, acetophenon glycolylhydrazin, glycolhydrazinacetacetic ester, glycolhydrazid-anhydride, hydrazoglycolid and its hydrochloride. In Treatise VI. Th. Curtius discusses the behaviour of hydrazin hydrate with phthalic acid and maleic anhydride. Then follows an experimental examination of phthalic hydrazid, its potassium, sodium, and silver compounds, its behaviour with benzaldehyd, with the mineral acids, and with bromine; diacetyl phthalhydrazide, methylphthalhydrazide, phthalhydrazidacetic ester, and phthalhydrazidacetic acid, its ammonium and diammonium compounds. Then follow experiments on the reduction and oxidation of phthalhydrazid, the action of maleic anhydride upon hydrazin hydrate silver- and copper- amidomaleinimides, acetylamidomaleinimid, maleinhydrazid, hydrazin maleiate, trimethylpyrazolin maleiate, trimethylpyrazolin chloride, and picrate and hydrazorin fumarate.

Researches from the Laboratory of the University of Freiburg, in Breisgau.—These consist of a paper by

Ad. Claus on kyaphenin and some substituted benzonitriles; and a memoir by Claus and Alf. Ammelburg, on meta-ana-dichlorquinolin.

Contributions to our Knowledge of Anethol.—C. Hall.—These contributions consist of a paper by C. Hall and G. Gärtner, on the action of bromine upon anethol.

Oxidation Experiments, with some Derivatives obtained by the Action of Ortho- and Para-toluolsulphone Chloride upon Amidic Substances.—J. Træger and P. W. Uhlmann.—The authors have experimented on the anilides of ortho- and para-toluolsulphonic acid; on the condensation of para-toluolsulphon chloride and para-amidophenol; on oxidations of the condensation-products obtained in the experiment last-mentioned; the condensation of para-toluolsulphon chloride and ortho-amidophenol, with meta-amido phenol, and with phenylhydrazin.

The Benzene Nucleus.—W. Vaubel.—In this paper the author considers the solubility in water of some constituted products of benzene and the acetylation of aromatic amidosulpho acids.

A Correction.—C. Schall.—The author protests against an erroneous view in a notice of his "Determinations of Vapour Densities" (*Berichte*, xxiii., 919 and 1701), given as far back as 1890.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxi., No. 1.

Researches on the Relations between the Degree of Fusibility and the Composition of the Ash of Coal.—Eugene Prost.—The phosphoric anhydride in some kinds of coal reaches 2.02 per cent, whilst in others it is as low as 0.26, and in others again it exists merely as traces. The localities of the coals are not given.

Mounds of Coal-Ashes and the Hardness of Waters.—It is certain that coal-ashes rich in soluble compounds must increase the hardness of any waters with which they may come in contact. It is therefore important that the deposits of ashes from furnaces should be placed as remote as possible from wells, reservoirs, &c.

MISCELLANEOUS.

Prof. Röntgen, of Würzburg, after a Lecture which he had delivered on the Crookes vacuum tube, was invested with the Order of the Crown (Kronen Orden), second class.

Action of Nitric Oxide on Ferrous Chloride.—V. Thomas.—If into a perfectly dry glass tube, containing anhydrous ferric chloride, we pass a current of perfectly dry nitric oxide, there are formed, according to the temperatures, two distinct compounds of nitric oxide and ferric chloride. At the same time there are disengaged abundant yellowish brown fumes, of a substance which is deposited on the colder parts of the tube, and much resemble iron oxychlorides. If the temperature is raised, we see the appearance of white lamellæ of ferrous chloride. If these are allowed to cool in a current of the gas they take a fine red colour, and absorb nitric oxide. The yellowish brown substance has the composition Fe_2Cl_4NO . The red substance corresponds in its composition to the formula $5Fe_2Cl_4NO$.—*Bull. de la Soc. Chim. de Paris*.

ERRATUM.—P. 27, col. 2, line 25 from top, should read as follows :—
“(b) Mercuric oxide, 3.5 grms.; glacial acetic acid, 20 c.c.; and water 100 c.c., are mixed together.”

MEETINGS FOR THE WEEK.

- MONDAY, Feb. 3rd.—Society of Arts, 8. (Cantor Lectures). "Alter-nate Current Transformers," by Dr. J. A. Fleming, F.R.S.
 — Medical, 8.30.
 — Society of Chemical Industry, 8. "Manufacture of Linoleum," by W. F. Reid, F.I.C.
 TUESDAY, 4th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.
 — Society of Arts, 8. "The Garden in relation to the House," by F. Inigo Thomas.
 — Institute of Civil Engineers, 8.
 — Pathological, 8.30.
 WEDNESDAY, 5th.—Society of Arts, 8. "The Mexican Drainage Canal," by F. H. Cheesewright, M.Inst.C.E.
 — Geological, 8.
 THURSDAY, 6th.—Royal, 4.30.
 — Royal Society Club, 6.30.
 — Royal Institution, 3. "Dante," by Philip H. Wicksteed, M.A.
 — Chemical, 8. "Molecular Weight and Formula of Phosphoric Anhydride and of Metaphosphoric Acid," by Prof. Tilden, F.R.S., and R. E. Barnett. "Lead Tetracetate and the Plumbic Salts," by A. Hutchinson, M.A., Ph.D., and W. Pollard, B.A., Ph.D. "An Improved Mode of Determining Urea by the Hypobromite Process," by A. H. Allen. "An Examination of the Products obtained by the Dry Distillation of Bran with Lime," by W. F. Laycock, Ph.D. "Luteolin," by A. G. Perkin.
 FRIDAY, 7th.—Royal Institution, 9. "Portrait Painting in its Historical Aspects," by the Hon. John Collier.
 — Geologists' Association, 7.30. (Anniversary).
 — Quekett Club, 8.
 SATURDAY, 8th.—Royal Institution, 3. "Realism and Idealism in Musical Art," by Prof. C. Hubert H. Parry, D.C.L., &c.

TO CORRESPONDENTS.

C, V.—Yes, to both questions.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1889.

CERTAIN PROPERTIES OF RÖNTGEN'S RAYS.

By JEAN PERRIN.

I WILL admit at once that I have had only very vague information drawn from the daily papers concerning Prof. Röntgen's discovery, and that I am still in ignorance as to the exact nature of his experiments.

However it may be, here are those which I have attempted.

I. I have first repeated that which constitutes the discovery: if we place, in presence of a Crookes's tube in activity, a photographic case charged and closed, on which are arranged different objects, and if in these develop the plate in the ordinary manner, we see appear the shadows of certain of these objects; *something* which emanates from the tube has impressed the plate through the interposed bodies. This is Röntgen's radiation.

These rays are not *kathode rays*; these latter cannot, in fact, issue from the vacuum tube except through a wall of some microns in thickness, whilst Röntgen's rays act easily out of a tube the side of which may have the thickness of 1 m.m.

II. I then collected some indications as to the degree of transparency of different substances.

Wood, paper, wax, paraffin, water, appeared very transparent, though the influence and thickness remained very distinct. Then come, arranged in the order of increasing opacity, coke, bone, ivory, spar, glass, quartz (either parallel or perpendicular to the axis), rock-salt, sulphur, iron, steel, copper, brass, mercury, lead. These results are still not numerous, and I cannot think of combining them by general law; still we may remark that the metals are in general less transparent than the substances, but have not the absolute opacity which they present for light. If, *e. g.*, we superimpose three plates of iron, each of about 0.2 m.m. in thickness, opacity appears only in the region covered by all three plates.

III. I then made a rather rough experiment in order to find if the radiation is well-defined, or if it merely forms a diffused tuft; in a word, I have examined if its propagation is rectilinear.

To this end I placed before the tube two diaphragms of brass (which is opaque), at the distance of some centimetres, on a sensitive plate placed a little further. I obtained a very definite spot with an umbra and a penumbra, and the dimensions of this spot agree with the hypothesis of rectilinear propagation.

It is therefore possible to isolate definite pencils, the properties of which will be studied.

IV. I have attempted the reflection of a pencil of Röntgen's rays, defined by two slits of 0.5 m.m. at the distance of 4 c.m. The pencil fell upon a mirror of polished steel at an angle of 45°, whence after reflection it could fall upon a filled frame. After an hour's exposure I obtained absolutely no impression.

The experiment was repeated with a plate of flint-glass as a mirror. The exposure was prolonged for seven hours, but absolutely nothing was obtained.

V. I attempted the refraction of Röntgen's rays. In the lower half of the pencil, defined by the system of slits, I interposed first a prism of paraffin of 20°, and a prism of wax at 90°. The two parts of the pencil should give distinct images if refraction took place; but the two images were prolonged exactly, and we may affirm that if any deviation exists it is inferior to 1°.

VI. Continuing to seek for some properties of Röntgen's

rays capable of co-existing with a rectilinear propagation, I attempted to form diffraction fringes.

The active part of the tube was placed before a very narrow slit; at 5 c.m. further was placed a slit of 1 m.m., and at 10 c.m. further the frame fitted and closed. The exposure was continued for nine hours. I obtained an image with very distinct margins, on which no fringe was perceived.

I placed, exactly at the place of the former plate, a second sensitive plate, and operated this time with an open frame, so as to receive the green light issuing from the tube. After some minutes this light gave a silhouette, exactly superimposed on the former, but on which fringes were seen.

If, therefore, the phenomenon is periodic, the period is much lower than that of the green light employed.

It is well to observe that this experiment, made very accurately, proves the rectilinear propagation of Röntgen's rays. Around this property which they possess more strictly than light are grouped those mentioned in this paper.

VII. Lastly, being curious to see what practical interest might attach to the silhouettes obtained, I experimented on some living tissues, with the assistance of M. Oigny, preparator of zoology at the Ecole Normale of M. Mouton, an *attaché* of the Museum. We have the honour of presenting to the Academy two proofs which represent very faithfully the skeleton and some organs of a flat-fish (*Pleuronectes*) and of a frog.

M. Poincaré made the subjoined remarks:—Professor Röntgen has already recognised that the X rays are not refracted; he has experimented with prisms formed of different materials; on one occasion only he thought that he observed a slight deviation, corresponding to an index of 1.05; but this observation remains doubtful. He has likewise seen that the rays do not undergo a regular reflection, but he believes that they may experience an irregular and diffusive reflection.—*Comptes Rendus*, cxxii., p. 186.

THE KATHODE RAYS.

By JEAN PERRIN.

Two hypotheses have been proposed to explain the properties of the kathode rays.

Some authorities think, with Goldstein, Hertz, and Lenard, that this phenomenon is due, like light, to the vibrations of the ether, or even that it is light with a short wave-length. Others, Crookes and J. J. Thomson, consider that these rays are formed of matter charged negatively and travelling with great velocity. From a paper courteously forwarded us by the author, we learn that, according to his experiments, the facts observed do not easily agree with the theory which regards the kathode rays as ultra-violet light. On the contrary, they are in harmony with the theory which regards them as a material radiation.

ON THE UTILITY OF PHOTOGRAPHS IN HUMAN PATHOLOGY TAKEN BY MEANS OF THE X RAYS.

By MM. LANNELONGUE, BARTHELEMY, and OUDIN.

THE communication of Oudin and Barthelemy on this subject has led us to undertake some researches with a view of confirming our first results, and also of ascertaining what advantage we may obtain by the employment of Röntgen's rays.

We have therefore undertaken the researches, the first results of which I am about to lay before the Academy.

Our appliances are as yet imperfect, and we are aware of our own inexperience.

The first fact is that of an anatomical case. It is that of a thigh bone attacked with osteomyelitis. One of us has shown elsewhere that the malady known under this name is wrongly considered as a periostitis.

If this were true the bony alterations would have produced themselves from the surface to the centre of the bone. The photograph shows, on the contrary, that the surface of the bone is intact, whilst the internal layers are destroyed as far as half a m.m. from the surface.

Normally the compact osseous tissue, here reduced nearly to the thickness of a piece of paper, should have at least half a c.m. in thickness. This has allowed it to be traversed by the light, and this is the cause of the white spots remarked on the bone.

The second photograph is that of a tubercular affection of the first joint of the middle finger of the left hand.—*Comptes Rendus*, vol. cxxii., p. 159.

PROOFS OBTAINED BY MEANS OF RÖNTGEN'S PROCEDURES.

By H. DUFOUR.

THE hand of a child, the fingers of which were garnished with rings of brass and aluminium, yielded a proof in which we distinguish the projection of the rings, the outline of the skin, the structure of the bones, and in particular the incomplete ossification of the last joint of the little finger.

The photograph of a frog permits us to distinguish the bones of the pelvis of the limbs, and to some extent those of the head.

The proof of a trough with parallel sides partly filled with blood, showed merely a scarcely perceptible difference of intensity between the empty portion and that occupied by the liquid.

Ch. V. Zenger addressed a note regarding the recent experiments of Professor Röntgen.

The author recalls attention to his own communications made to the Academy of Sciences in February and August, 1886; the photograph of Mont Blanc which he obtained by night at the distance of 80 kilometres. He also drew attention to the researches of Hittorf, Hertz, and Ayrton, who have shown the permeability of plates of sulphur, vulcanite, plaster, &c. According to him the kathode radiation is merely the invisible ultra-violet radiation produced in the rarefied space of the Crookes tubes, and it has been already demonstrated that it is arrested by metallic plates. These radiations can develop fluorescence and phosphorescence in bodies which are opaque to the radiations of greater wavelengths.—*Comptes Rendus*, vol. cxxii., p. 213.

LUTEOL: A NEW INDICATOR.

By W. AUTENRIETH.

THIS substance is oxychloridiphenylquinoxalin, and has received the above name because it is a phenol, and takes in contact with alkalis an intense yellow colour. For its preparation we heat 1 mol. ethoxyphenylendiamine with 1 mol. benzil to ebullition, in an alcoholic solution. We thus obtain a crystalline precipitate of ethoxyphenylquinoxaline. This substance, fusible at 150°, is re-crystallised from alcohol, and, heated with phosphorus pentachloride to 70° to 90°, in a paraffin bath, when by atoms chlorine enters into combination, whilst phosphorus trichloride and hydrochloric acid distil over. The ethoxychloridiphenylquinoxalin is then heated with hydrochloric acid to 180° to 200°, in a sealed tube, when alkyl is split off in the form of ethylen-chloride. The substance thus obtained is repeatedly re-crystallised from alcohol.

The fine, woolly, yellowish needles melt at 246°. At higher temperatures they sublime without decomposition. Luteol is insoluble in water, sparingly soluble in cold alcohol, but readily soluble in hot alcohol and in ether. Concentrated sulphuric acid dissolves luteol with a red colour, but it is re-precipitated by water. In concentrated hydrochloric acid it is sparingly soluble, but perfectly insoluble in the same acid if dilute. Alkalies dissolve it readily with a yellow colour. Luteol expels carbonic acid from the carbonates, and the acid character of the phenol is much increased by the introduction of an atom of chlorine. The sensibility of the change of colour is very great. If we add a drop of dilute soda-lye to 1 litre of water, and take 5 to 10 c.c. of the liquid, it is turned very distinctly yellow by the addition of a few drops of an alcoholic solution of luteol. Hence its sensitiveness is very decidedly greater than that of phenolphthalein and litmus. As compared with phenolphthalein it has the advantage of being applicable in presence of ammonia. It has the advantage over litmus because no intermediate colours appear in the change.—*Zeitschrift für Analytische Chemie*, xxxv., p. 68.

DIRECT COMBINATION OF THE NITROGEN OF THE ATMOSPHERE TO METALS IN THE STATE OF MAGNESIUM, ALUMINIUM, IRON, COPPER, &c., NITRIDES.

By A. ROSSEL.

IN the researches conducted for fixing the nitrogen of atmospheric air, several *savants* have succeeded in combining, in small proportions, this element, which in general possesses a very feeble activity.

James Pellat Rickman, in 1878, described an apparatus which rendered it possible to combine small quantities of nitrogen by heating coke with a fixed base in contact with air. Spongy platinum at high temperatures converts a small quantity of the nitrogen of the air into nitrous products, but in these two cases no analysis shows the exact figures.

Wigled and Geuther, in a remarkable investigation, demonstrated the affinity of magnesium for pure nitrogen, and described for the first time the compound Mg_3N_2 , which has recently played an important part in the discovery of argon by Lord Rayleigh and Prof. Ramsay.

M. Mallet has observed that magnesium, when burning slowly in air, yields not merely magnesium oxide, but a grey powder composed of magnesium and nitrogen.

M. Méry, of Zurich, has verified this fact, and found that, on heating magnesium to redness in a very weak current of air, there are formed small quantities of nitrogenous product.

Finally, C. Hinkler has shown that, on preventing the rapid oxidation of magnesium in air, by mixing it with magnesia there is formed a larger proportion of magnesium nitride.

In some studies on the reductive power of magnesium and aluminium, with which I have reduced at dull redness the metaphosphates which give off their phosphorus in a pure state, I have ascertained that there are formed secondary products containing small quantities of combined nitrogen. But whilst studying the important researches of H. Moissan, I came upon the most curious reaction concerning the combination of the nitrogen of atmospheric air in presence of oxygen.

In his work on the properties of calcium carbide, Moissan has shown that at high temperatures the metals have no action upon calcium carbide.

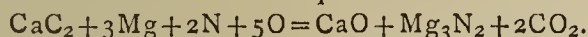
In concert with Léon Frank, I have found that it is not alike when we heat pulverised calcium carbide in powder with pulverised magnesium in a porcelain crucible, or in a tube in which there is a free circulation of atmo-

spheric air at the temperature of dull redness. The reaction takes place in a regular manner if we place in layers pulverised calcium carbide, and magnesium finely powdered, in a porcelain crucible.

On heating the open crucible with the flame of a Bunsen burner, there soon appears a flame produced by the combustion of the carbon of the carbide, which gives rise to carbonic acid, and the calcium burns, producing calcium oxide. At this moment there ensues a lively incandescence, and, after cooling, the magnesium is almost totally converted into magnesium nitride.

The analysis of this product, which can be mechanically separated from the calcium, leads to the formula Mg_3N_2 ; the mixture of the residue in the crucible contains up to 23 per cent of nitrogen taken from the atmospheric air.

This reaction leads to the equation—



On mixing the contents of the crucible with water, there ensues a brisk effervescence with liberation of ammonia—



Aluminium, zinc, iron, and even copper, if mixed in fine powder with calcium carbide and heated in the air, give similar reactions.

There are formed nitrogenous products decomposable by water, and more easily by dilute caustic potassa.

These reactions, as M. Moissan has pointed out, are an additional proof that at the epoch of the formation of the earliest geological strata nitrogen did not exist in the free state, but in combination with metals.—*Comptes Rendus*, cxxi., p. 941.

THE SIZE OF ATOMS.

By HAROLD A. WILSON, Senior Akroyd Scholar,
The Yorkshire College, Leeds.

THE estimate of atomic dimensions depending on the surface energy of water and its latent heat of evaporation is well known. A quantity of water is supposed to be drawn out into a film of such an area that the work done in extending it is equal to its latent heat of evaporation. Take one gram. of water; then if A is the area required, we have $2A \times 86 = 600 \times 42 \times 10^6$; for 86 = the number of ergs per sq. c.m. of water surface at $0^\circ C.$, and 600 = the latent heat of evaporation of 1 gram. of water at $0^\circ C.$, therefore,—

$$A = 1.5 \times 10^8 \text{ sq. c.m.}$$

The thickness of the film is, therefore,—

$$\frac{1}{A} = 0.7 \times 10^{-8} \text{ c.m.,}$$

and this is taken as an approximation to the diameter of a molecule of water.

The data employed in the above calculation may be used to estimate the diameter of a molecule of water in another way, which, however, leads to a result of the same order of magnitude.

The pressure inside a bubble is given by the formula—

$$P = \frac{4T}{R};$$

where T = surface-tension of the water, and R = radius of the bubble. Suppose a bubble so small that the pressure in it is just double the internal pressure in water due to the attraction between the molecules; then its radius may be taken as an estimate of the diameter of the molecule (*i.e.*, the mean distance between the centres of the molecules). For if we suppose such a bubble, consisting of molecules of water only, to be submerged in water, then as the water molecules close round it its equilibrium will not be disturbed, because the pressure in it is already double that in the interior of the water, so that the space

within it will evidently be no greater than that usually between the molecules of the water.

The internal pressure in water is 1.3×10^{10} dynes per sq. c.m., as usually calculated thus:—The work required to bring a gram. of water into a water surface is put equal to half the latent heat of evaporation. This gives—

$$(p_1 - p_2)v = \frac{1}{2} \times 600 \times 42 \times 10^6 \text{ ergs};$$

where p_2 = internal pressure,

p_1 = pressure in the surface = one atmosphere,

v = volume of 1 gram. of water.

$$\therefore p_2 = \frac{1}{2} \times 600 \times 42 \times 10^6 = 1.3 \times 10^{10}.$$

For the radius of the small bubble then—

$$\frac{4T}{R} = 1.3 \times 10^{10} \times 2,$$

$$\therefore R = \frac{4 \times 86}{1.3 \times 10^{10} \times 2} = 1.3 \times 10^{-8} \text{ c.m.}$$

Surrounding a bubble with water of course halves the pressure in it since it destroys one surface, and therefore the pressure in the bubble is taken as being double that in the water.

The above may be more simply expressed as follows:—The pressure in a spherical air bubble under water is given by $\frac{2T}{R}$. Now, consider the molecules in a liquid,

they are believed to be some distance apart, and the cavities between them may be supposed to have an average radius equal to their distance apart or diameter as above defined. Supposing the formula just given to apply to these cavities, we get $\frac{2T}{R} = p_2$, as before.

An estimate of the diameter of a molecule may also be obtained by considering the diminution of vapour pressure which occurs when a water surface is curved. The effect of curving the surface is to slightly more completely surround any molecule in the surface with other molecules. This increases the work necessary to force a molecule out, and so diminishes the average velocity of the molecules which escape. Assuming as a rough approximation that, with a spherical surface, the resistance to an escaping molecule is proportional to the angle, in a plane perpendicular to the surface of the liquid, subtended by the nearest other molecules when the molecule is at the surface we get—

$$\frac{\alpha}{\pi} = \frac{p_2 - p_1}{p_2};$$

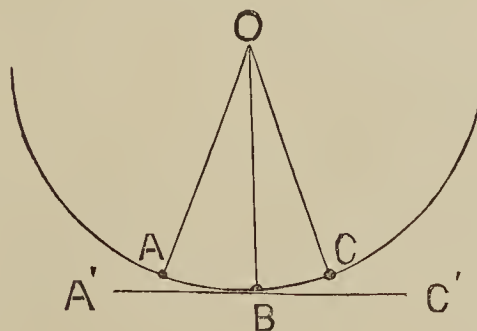
where $\pi + \alpha$ = the angle just mentioned,

p_2 = pressure with concave surface,

p_1 = pressure with plane surface.

Let $A B C$ be three molecules in the surface, and O the centre of the sphere formed by the surface, then—

$$\angle C'BC = \frac{1}{2}\alpha = \angle BOC;$$



but—

$$BC = OC \times \angle BOC = OC \times \frac{\alpha}{2} =$$

the distance between the molecules. Let $OC=r$, and the distance between the molecules d , then $d=\frac{1}{2}r\alpha$; but

$$\alpha = \pi \cdot \frac{p_2 - p_1}{p_2} \therefore d = \frac{\pi r}{2} \cdot \frac{p_2 - p_1}{p_2}.$$

But we have that—

$$\frac{p_2 - p_1}{p_2} = \frac{2T\sigma}{p_2 r \rho};$$

where σ = density of the water vapour,
and ρ = density of the water,

$$\therefore d = \frac{\pi T \sigma}{p_2 \rho}.$$

At 0°C . this gives roughly, since then,—

$$\sigma = \frac{5}{10^6} \frac{\text{grm.}}{\text{c.m.}^3} \text{ and } p_2 = 6 \times 10^3 \frac{\text{dynes}}{\text{c.m.}^2}$$

$$d = \frac{3.1 \times 86 \times 5}{6 \times 10^3 \times 10^6} = \frac{2.2}{10^7} \text{ c.m.}$$

We should expect this result to be large, because it is evident that the resistance to an escaping molecule will increase less rapidly than the angle $\pi + \alpha$ when α is small. Considering the nature of the assumptions made in the above estimations, the results are remarkably concordant, and seem to me to afford some additional confirmation of the limits 10^{-8} to 10^{-7} c.m. for the diameter of a molecule of water.

ON THE PRESENCE OF SODIUM IN ALUMINIUM PREPARED BY ELECTROLYSIS.

By HENRI MOISSAN.

THE experimentalists who have occupied themselves with the properties of aluminium have often arrived at contradictory results. It has been the same when, on account of its low specific gravity, some countries have tried to use it for the manufacture of articles for the small equipment of infantry, such as drinking-cups. Sometimes the metal has behaved well, and shown properties which have caused its use to be advocated, but sometimes, on the contrary, its employment has led many to disappointment.

These difficulties depend on the difference of composition of industrial aluminium. We have already shown (*Comptes Rendus*, cxix., p. 12) that the metal may contain nitrogen and carbon, and that under these conditions its properties are remarkably modified. Its breaking and extension-weight decrease rapidly. Having had the opportunity of analysing aluminium obtained from the three great works at present established at La Praz (France), Neuhausen (Switzerland), and Pittsburg (United States), we have recognised a new impurity which seems to have a great importance as regards the preservation of the metal. We refer to the presence of sodium in industrial aluminium.

We may demonstrate the existence of sodium in some aluminums in the following manner:—We take 250 grms. of filings carefully prepared, which are placed in an aluminium bottle along with 300 c.c. of distilled water obtained in a metal still. The mixture was then left to itself for two weeks, heating it to ebullition every day. It was then thrown upon a filter, washed with boiling water,* and the filtrate, which is slightly alkaline, is evaporated to dryness in a platinum capsule. It is heated to dull redness, when the mass turns brown. We add pure hydrochloric acid diluted with water, when there takes place a distinct escape of carbonic acid. The liquid is again evaporated to dryness and heated to about 300° to expel any excess of hydrochloric acid, when we obtain a residue having all the characters of sodium chloride. We take

* In this experiment we often obtain a small quantity of soluble alumina, analogous doubtless to colloidal alumina which has passed through the filter and which is then precipitated.

up the residue in water and determine the chlorine as silver chloride. From the weight of this latter compound we deduce the quantity of sodium removed by water from the aluminium filings.

When making the complete analysis of the metal we have found sodium in a number of specimens of aluminium. The proportion of sodium varies between 0.1 and 0.3 per cent. An aluminium prepared some time ago by the firm of Bernard contained 0.42 per cent.

When an aluminium contains a small quantity of sodium it is attacked by cold water at first slowly, but then the action proceeds with increasing intensity. In fact, if a small volume of water, not renewed, exists in presence of a leaf of such an aluminium, we see at first a slight layer of alumina forming upon the metal. Some days afterwards the liquid has an alkaline reaction with litmus paper. After this the reaction becomes more rapid. At every point where the aluminium contains sodium there is produced a little alkali, which reacts upon the metal so as to form an aluminate. This sodium aluminate is then dissociated by water with a deposition of alumina and a formation of soda, and when the liquid is slightly alkaline we understand how the decomposition becomes much more active.

The alloys which we may prepare with an aluminium will therefore possess quite different properties according as they contain or do not contain a small quantity of sodium.

The presence of sodium in industrial aluminium shows that the electrolysis of the mixture of cryolite and alumina gives rise to a number of secondary reactions in which the sodium may play a different part according to the composition of the bath and the intensity of the current.

It is thus that M. Riche, in a study of the alloys of aluminium and tin, has shown that these alloys decompose water at the ordinary temperature (*Journal de Pharmacie*, Series 6, vol. i., p. 5). I have succeeded in forming an alloy with 6 per cent of tin containing aluminium quite free from sodium, and under these conditions, after remaining two months in common water, the metal became spotted in several places, yielding small efflorescences of alumina, but not producing any escape of gas. My aluminium free from sodium was alloyed with 6 per cent of tin, avoiding the action of nitrogen and of the furnace gases, for M. Franck has proved that at a red heat aluminium decomposes carbonic acid, and even carbon monoxide. We thus obtain an alloy which, if rolled under a strong pressure, gave—

Tempered.—Resistance, 17.6; elasticity, 8.20; extension, 20.

Compressed.—Resistance, 23.43; elasticity, 22.90; extension, 6.

A leaf of this metal was divided into two parts. The first part was placed in Seine water, which was aerated daily by agitation. The second part was placed in a beaker of Bohemian glass in Seine water covered with a layer of oil several c.m. in thickness. The mean temperature of the laboratory was close upon 20° . The experiment was commenced on September 30, and was continued for two months. In this time the aluminium was covered with white efflorescence. It was spotted over almost its entire surface, but in neither case no bubble of hydrogen escaped. The specimen in the agitated water was oxidised the more rapidly.

This experiment was made only with an alloy containing a low proportion of tin. M. Riche has shown that with high proportions the decomposition of water becomes very active, and has thus established the reason which makes us reject every attempt at soldering with an alloy containing tin.

Aluminium is a metal which, if carefully tempered, works very well by means of rolling or stamping.

M. Riche informs me also that he has detected the presence of sodium in some samples of aluminium.

M. Meissonier, Chief Pharmacist at the Military

Hospital of Saint Martin, who has undertaken prolonged researches on this subject, has even met with a sample of aluminium containing 4 per cent of sodium.

There is another important point on which we must insist regarding alloys of aluminium, those especially of copper. Every alloy which is not homogeneous is very difficult of preservation.

Dumas, in his memoir on the equivalent of aluminium, insisted on the non-homogeneity of aluminium prepared by the procedure of Deville.

We have had the opportunity of ascertaining, in moulded articles, the bad effects of a want of homogeneity. If we leave distilled water in such a vessel, we see in about a fortnight the appearance of small white spots of hydrated alumina. Each spot is surrounded with a brilliant halo, it continues to increase, and if we cut off the part attacked and remove the hydrated alumina, we generally distinguish with the microscope a small particle of carbon or of some other substance which has formed an element of a galvanic couple, and which has disaggregated the metal over a greater or smaller surface. If, instead of letting the water remain on this non-homogeneous aluminium, we leave on the surface a saturated solution of sodium chloride, the phenomenon is intensified, and each particle of carbon produces an attack of the aluminium foil sufficient to perforate it.

This formation of small battery elements over the surface of the aluminium is the chief cause of the deterioration of the metal.

On the other hand, with a metal quite homogeneous, containing neither nitrogen, carbon, nor sodium, there is no point of attack, and the water which has remained upon the metal retains all its clearness and contains no alumina.

The same phenomena appears with alcohol diluted with water, *e.g.*, rum, and in case of aluminium of bad quality it explains the attack of certain vessels—an attack which sometimes takes place with very great energy.

I must remark, in conclusion, that aluminium, having a great disposition to form couples with every other metal, should never be used except alone.

A particle of iron or brass, on contact with aluminium, will always in a short time effect the oxidation of the metal and its conversion into alumina. All industrialists who have had to operate upon large surfaces of aluminium have observed, at their own expense, the generality of this decomposition.

In this research, conducted from a chemical point of view, we have not needed to insist on the importance of tempering in rolling and stamping aluminium. Without this precaution, the metal easily breaks and becomes unfit for any use.—*Comptes Rendus*, cxxi., p. 794.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING DECEMBER 31ST, 1895.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, *Metropolis Water Act*, 1871.

London, January 10th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Dec. 2nd to Dec. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Com-

bustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined all were recorded as clear, bright, and well filtered.

The rainfall at Oxford during the month has been 2·08 inches, as against 2·10 inches, the average for the past 25 years; this shows a slight decrease, *viz.*, 0·02 inch as compared with the average.

The rainfall for the year 1895 is detailed in the following table:—

	Actual fall.	Mean of 25 years.	Deficiency.	Excess.
January.. ..	2·60	2·26	—	0·34
February	0·21	1·92	1·71	—
March	1·46	1·59	0·13	—
April	1·78	1·78	—	—
May	0·16	1·95	1·79	—
June	1·12	2·21	1·09	—
July	3·41	2·58	—	0·83
August	2·28	2·24	—	0·04
September	0·57	2·66	2·09	—
October	2·85	2·56	—	0·29
November	4·17	2·31	—	1·86
December	2·08	2·10	0·02	—
	22·69	26·16	6·83	3·36

There is thus a deficiency of 3·47 inches, which has chiefly occurred during the months of February, May, June, and September.

Our bacteriological examinations for the month of December give the following numbers of colonies per c.c.

	Colonies per c.c.
Thames water, unfiltered	3259
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	110
Ditto ditto lowest	46
Ditto ditto mean	74
New River water, unfiltered	3933
New River water, from the Company's clear water well	65
River Lea water, unfiltered	3610
River Lea water from the East London Company's clear water well	64

These results show that the filtering arrangements of the Companies are highly satisfactory.

All the samples of water examined during the course of the past month gave satisfactory results; the amount of organic carbon shows a diminution, as compared with last year's report for the same period.

On the whole, during the course of the year, the London water supply has improved in quality.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

Melting- and Solidification-points of some Acids of the Fatty Series.—G. Massol.—The author has examined the propionic, valerianic (normal), isobutyric, and isovalerianic acids. They present distinctly the phenomena of superfusion; normal valerianic acid offering the greatest resistance to solidification. Of all the normal fatty acids at present known, valerianic acid melts at the lowest temperature (−58·5°). Among the abnormal, it is the isobutyric acid (−79°).—*Bull. de la Soc. Chim. de Paris*.

CHEMICAL RESEARCHES AND SPECTROSCOPIC
STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 52.)

CHAPTER V.

CHEMICAL RESEARCHES ON CARBONATE, OXALATE, SULPHATE, AND CHLORIDE OF CALCIUM.

SOME considerable time ago I tried to determine the atomic weight of calcium. I did not publish these researches, on account of the want of concordance in the results. At that time I tried to prepare some carbonate of calcium, both from chloride and pure nitrate, to compare its combining ratio with oxide of calcium, with that of Iceland spar. I found then that precipitated carbonate, and the same carbonate dissolved in water charged with carbonic acid, both retained water, a fact which is now generally known; besides this, I found that, when taking count of the water, carbonate which had been dissolved in water charged with carbonic acid, left—on calcination, in a platinum boat, put in a porcelain tube, traversed by a current of pure air—less oxide of calcium than the carbonate precipitated by sesqui-carbonate of ammonium, and also than the purest Iceland spar.

The atomic weight of calcium, as deduced from the artificial carbonate when re-dissolved in water containing carbonic acid, is nevertheless slightly greater than the figure required on Prout's hypothesis. The researches I have undertaken during the last few years have acquainted me with the difference in the composition of the calcic carbonates I prepared. I effected the decomposition of chloride and nitrate of calcium in glass vessels, by sesqui-carbonate of ammonium. It was by this means that I took up silicon and sodium from the glass, and combined it with the calcic carbonate formed. Having kept part of the salts made at that time, I was able to detect the presence of silica, not only in the carbonate precipitated directly, but also in the carbonate re-dissolved in water charged with carbonic acid.

All these researches had to be taken up again. The details into which I have entered will enable any one who desires to determine the atomic weight of calcium, to procure an oxide of this metal which I believe to be pure.

To satisfy myself of the identity of the calcic oxide, I had resource, successively, to the following natural or artificial compounds of calcium:—Colourless and transparent calc-spar and arragonite,—white marble,—and artificial oxalate, sulphate, and carbonate, made from nitrate which was prepared from Iceland spar. I submitted the calc-spar, arragonite, and white marble to the same treatment, to eliminate foreign bodies from them. I found silica, sodium, iron, and manganese in them all; traces of lithium, but neither strontium nor barium, in the Iceland spar; traces of lithium and magnesium, a notable quantity of strontium, but *not a trace of barium*, in the arragonite; and in the white marble, also, lithium, magnesium, and strontium, *without* barium.

Of all these foreign matters the elimination of sodium and strontium alone presented any difficulty.

Treatment of Iceland Spar.—Before commencing to separate the silica in a platinum vessel, which was sensibly attacked by *melted* nitrate of calcium, I had to effect the solution of the calcic carbonate by means of dilute hydrochloric acid, taking care to leave a small quantity undissolved. The chloride solution was boiled, in order to drive off the excess of carbonic acid, and then separated from the excess of carbonate used. Into the boiling liquid was poured, until it gave a decided alkaline reaction, some milk of lime reduced from oxide of calcium, which was made by calcining Iceland spar in a platinum vessel. After cooling it, the chloride solution was filtered; pure sal ammoniac was then added, it was evaporated to dryness in a platinum retort, and the residue was heated till

it gave off an abundance of chloride of ammonium fumes, *the only method known to me for eliminating silica*, the quantity of which was from 1-7000th to 1-8000th of the weight of Iceland spar.

The chloride of calcium, which still contained chloride of ammonium, was dissolved in water, and the solution, having been left to settle, was filtered to separate the free silica. The filter-paper used had been washed with very dilute hydrofluoric and hydrochloric acids, and then with pure water.

I twice evaporated the solution of chloride of calcium to dryness, raising the temperature high enough to volatilise each time part of the chloride of ammonium dissolved in the water on the first occasion; the absolute clearness of the liquid being doubtful, I filtered it. The second solution was perfectly clear. After being filtered again, it was diluted with as much pure water as the platinum vessels would hold, and gradually poured into a supersaturated solution of sesqui-carbonate of ammonium, which was both made and kept in a large platinum vessel under a bell-jar. After twelve hours' rest the supernatant liquid was decanted, the carbonate of calcium was put into a large covered platinum retort, and I washed the precipitate with cold water by decantation, using each time a quantity of pure water double the apparent volume of the carbonate. Fifteen washings with cold water were required to yield a decanted liquid which did not turn red litmus-paper blue. When this stage was reached, the washings still sensibly clouded an acid solution of nitrate of silver.

The washing was done by keeping the precipitate in suspension in boiling water, which was renewed until the liquid, having settled and been poured off, no longer clouded an acid solution of nitrate of silver. Twenty washings in boiling water were required to reach this stage. The carbonate was then dried in the same vessel.

Whenever I used the retort I took care to put on its lid, to prevent the dust of the air from falling into it.

I submitted the carbonate derived respectively from Iceland spar, arragonite, and white marble, to the following investigation:—

Carbonate from calc-spar, when taken straight from the retort on a recently heated platinum dish, turned an oxy-hydrogen blowpipe very slightly yellow. After heating it for fifteen minutes, during which time the surface of the thick coat of oxide was being renewed, spectrum analysis did not show the sodium spectrum more strongly than it could be seen in a blowpipe burning in the surrounding air.

The spectrum of calcium is described in the next chapter. This oxide, when heated to the fusing-point of iridium, does not show, after it has been reduced by volatilisation to the one-hundredth of its original mass, any trace of the spectra of lithium, strontium, or barium.

As regards sodium, the carbonates derived from arragonite and white marble behave exactly like that derived from calc-spar. On heating to a sufficiently high temperature, and maintaining it for some time, the resulting oxide easily frees itself from sodium. But it is necessary to heat the oxide of arragonite to the fusing-point of platinum, and the oxide of white marble to the fusing-point of iridium, in order to see the characteristic lines of strontium with the calcium spectrum. These experiments enabled me to prove with certainty the double influence of mass and temperature on the appearance or non-appearance of the spectrum of metals present.

I have not seen the spectrum of lithium in the vapour of the oxides of calcium from calc-spar, arragonite, and white marble. *I have only found traces of lithium in the filtrates of chlorides made by means of bicarbonate of ammonium.* All these liquids contain chloride of sodium. I was unable to detect the presence of chloride of potassium.

Although carbonate of calcium derived from Iceland spar showed no trace of the characteristic strontium lines, nevertheless I submitted it, as well as the carbonates ob-

tained from arragonite and white marble, to a similar treatment, to separate from it the strontium it might contain. For this purpose I followed Stromeyer's method.

I dissolved the carbonate, which had been precipitated and washed in pure nitric acid, in a platinum vessel. The solution was quickly evaporated down to a syrupy consistency, and the nitrate was then completely dried by putting the covered platinum retort into an air-bath, heated to between 150° and 170° .

Unless the dehydration is performed with the greatest care, the resulting salt is very basic, and it attacks the platinum, colouring the nitrate yellow. By some preliminary experiments I satisfied myself that, when the nitrate contains the least trace of water, absolute alcohol, when dissolving it, takes up strontium that cannot be precipitated by the addition of anhydrous ether. There is no question as to which is the lesser evil.

The dehydration being finished, the nitrate was taken up with the least possible quantity of absolute alcohol, and the cloudy solution was poured into a glass flask with a ground-glass stopper, and anhydrous ether added until the nitrate of calcium was precipitated. After the liquid had cleared, the flask containing it was put into a freezing mixture of sea-salt and ice. The liquid, becoming clouded afresh, was left in the freezing mixture until it became quite clear once more.

The clear and colourless supernatant liquid was most carefully decanted, so as not to disturb the precipitate, and it was filtered through a purified filter-paper, in a covered platinum funnel, and evaporated on a bath in a platinum vessel covered by a funnel larger than itself.

The deposit at the bottom of the flask was taken up by a mixture of equal volumes of absolute alcohol and ether, and poured into the filter used for filtering the bulk of the liquid. *The etherised alcohol used to exhaust the insoluble mass was entirely separated.*

I carefully examined the residue left by the nitrate of calcium made from Iceland spar, arragonite, and marble. The results I arrived at were as follows:—

The granular residue left, after treating spar, consisted entirely of basic nitrate of calcium, with traces of platinate of calcium, but no trace of nitrate of strontium. In fact, its oxide, when heated in an oxy-hydrogen blowpipe to the fusing-point of sodium, showed persistently and exclusively the calcium spectrum.

The granular residue left, after treating arragonite, consisted of a mixture of basic nitrate of calcium, slightly tinted yellow by platinate of calcium, and a noticeable amount of nitrate of strontium, recognisable in an oxyhydrogen blowpipe when the mixture of oxides is only treated to the fusing-point of platinum.

The granular residue left, after treating white marble, also consisted of a mixture of basic nitrate of calcium and nitrate of strontium, tinted by traces of platinate of calcium. The nitrate of strontium was very considerably less in quantity than in the arragonite.

Having found no trace of strontium in the nitrate of calcium from the Iceland spar used, I used it for preparing carbonate, oxalate, and sulphate of calcium, for the purpose of satisfying myself as to the identity of the oxide of calcium made from these salts. I shall return later on to this subject.

The solution of nitrate of calcium derived from arragonite and marble, from which the strontium had been eliminated as described above, was evaporated afresh in the platinum retort, and the residue most carefully dehydrated. I then repeated the whole treatment of the dried nitrate and the residue, with alcohol and anhydrous ether.

I found, beyond a doubt, the presence of strontium, *but in a very small quantity*, in the residue left by the nitrate derived from arragonite. I only found basic nitrate of calcium, tinted yellow by platinate of calcium, in the residue left by the nitrate derived from marble.

The solution of nitrate from arragonite was evaporated a *third* time, and the salt, when dried and entirely dehy-

drated, was again treated with etherised absolute alcohol. I was not able to detect, in the residue left by this third treatment, the presence of the slightest trace of strontium, when testing for it in an oxyhydrogen blowpipe at the fusing-point of iridium.

Thus, although nitrate of strontium may not be absolutely insoluble in an alcoholic and etherised solution of nitrate of calcium, as is easily ascertained, we can, nevertheless, eliminate the strontium, thanks probably to the formation of a basic nitrate of calcium, which is quite insoluble in etherised alcohol.

The nitrates of calcium from arragonite and marble, when freed from strontium, were converted into carbonate, just as I have described for the nitrate derived from Iceland spar.

I purified about 350 grms. of *colourless* and *transparent* Iceland spar.

The nitrate made by the method described above was divided into three parts, A, B, and C. The first, A, was converted into carbonate; the second, B, into oxalate; and the third, C, into sulphate, and partially into carbonate.

I effected the conversion into carbonate in platinum vessels, by means of sesqui-carbonate of ammonium, as I have described above, with reference to chloride of calcium. The carbonate was washed and dried in the same way, and with the same care. It is useless to repeat these details. I converted the second third, B, into oxalate, using an oxalate of ammonium which had been repeatedly crystallised in a *platinum* dish until 10 grms. of it, after calcining, left no weighable residue, which takes longer to effect than is generally believed, when dissolving the salt in water containing some thousandths parts of sesqui-carbonate of ammonium, and which, in my opinion, it is impossible to do in glass vessels.

To precipitate it, I slowly poured the solution of nitrate of calcium, when *cold*, into a saturated solution of oxalate of ammonium, having in suspension enough of this salt to convert all the nitrate of calcium used into oxalate. I did this so as not to have a greater volume of filtrate than I wished to examine with the first two washings, to see whether they contained any foreign solids.

After being undisturbed for twelve hours, the filtrate was decanted and passed through a purified filter-paper in a platinum funnel, and the oxalate of calcium was put into twice its own volume of water.

The filtrates were evaporated to dryness in a platinum dish, together with the first two washings.

The product of evaporation of the filtrates and washings, consisting of nitrate and oxalate of ammonium, was heated so as to drive off all volatile bodies. There remained a residue of oxide of calcium, weighing 0.041 gm., very strongly coloured yellow by platinate of calcium, and showing a very decided sodium spectrum, without a trace of a potassium or lithium spectrum.

The oxalate of calcium was washed by decantation. It was washed twenty times, using each time twice its volume of water; after being washed, the salt was dried on a water-bath, and converted into carbonate by raising it to a dull-red heat in the platinum dish which held it. I shall refer further on to this carbonate, which was quite *white*.

When introduced immediately after its preparation on a recently heated platinum dish, with an oxyhydrogen blowpipe, it coloured it yellow; this colour almost instantaneously changed to orange-red, and became deep red at the fusing-point of platinum. After the sodium was completely eliminated by exposing a new surface, the oxide of calcium spectrum shown was identical with that of oxide from the carbonate made from chloride and nitrate of calcium.

The last third, C, of the solution of nitrate of calcium from the spar, was converted into sulphate by pouring it into a quantity of absolute alcohol, acidulated with pure sulphuric acid. After the sulphate of calcium was deposited, I decanted the alcoholic filtrate, and turned the

precipitate into twice its own volume of alcohol at 60°, pouring it all into a platinum funnel provided with a clean linen plug, connected with a water-pump, passing weak alcohol through it so long as the washings turned blue litmus-paper red.

Directly after it was washed, the precipitated sulphate of calcium did not colour yellow either a Bunsen or a hydrogen flame, and showed no trace of the sodium spectrum. Of all the calcium compounds, the sulphate was the only one which showed this characteristic on being put into a flame. This fact was more surprising, because there is a double sulphate of calcium and sodium.

(To be continued.)

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 16th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. A. J. Chapman, H. W. Dickinson, G. Goldfinch, E. Grossman, and A. F. Theodosius were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Henry Bentley, B.Sc., 116, Yarrowburgh Street, Moss Side, Manchester; Joseph John Bowley, 34, Elm Park Road, Chelsea; Daniel Bray, Broadmoor, Cinderford; Hugh Charles Herbert Candy, B.A., B.Sc., 101, Gower Street, W.C.; Thomas Ewan, B.Sc., Ph.D., Yorkshire College, Leeds; Charles James Pemeller Fuller, Mona House, Horwich, Lancs.; William Harrington, 11, Edgehill, Whitehaven; Albert Howard, 17, Elthron Road, Fulham, S.W.; Ernest Haynes Jeffers, 50, St. John's Hill Grove, New Wandsworth, S.W.; James Johnstone, Braehead, Parkhill, Rutherglen; Charles Edward Sage, 7, Oseney Crescent, N.W.

Of the following papers those marked * were read:—

*1. "*The Acetylene Theory of Luminosity.*" By VIVIAN B. LEWES.

The author points out that in 1882 Professors Dewar and Liveing (*Proc. Roy. Soc.*, xxxiv., 438) came to the conclusion that the "formation of acetylene in ordinary combustion seems to be the agent through which a very high local temperature is produced," whilst Guequen (*Trans. Société Technique*, 1884) claims to have put forward the acetylene theory of luminosity in 1884.

The author considers that the criticism offered against the acetylene theory by Smithells (*Trans.*, 1895, lxvii., 1049) in no way affects the considerations upon which the theory is based, which are—

1. That the unsaturated hydrocarbons in the inner region of the flame are largely converted into acetylene before luminosity commences.
2. That acetylene develops luminosity when heated whilst flowing through a hard glass tube, no air being present.
3. That the temperature necessary to decompose acetylene with evolution of light does not raise to incandescence the carbon liberated by the decomposition.
4. That in luminous hydrocarbon flames of sufficiently high temperature the luminosity varies directly with the amount of acetylene present at the point where luminosity commences.

The objections raised by Smithells against the determination of absolute temperatures in flames by means of the Le Chatelier thermo-couple are warmly endorsed by the author as far as those portions are concerned in which combustion is taking place, and these objections were pointed out in his former paper (*Proc. Roy. Soc.*, lvii., 452), but he contends that the results obtained in the

inner non-luminous portion of a hydrocarbon flame are probably fairly accurate, and the results obtained by Smithells fully confirm the statement that the temperature in the inner zone rises from a comparatively low temperature close to the burner to over 1000° at the apex of the zone.

The author describes experiments showing that although the heat of combustion of acetylene is very high, so small a proportion has to be burnt in order to develop the remaining energy as light and radiant heat that it by no means follows that the acetylene flame is hotter, or even as hot, as a coal-gas or ethylene flame of the same size.

Smithells has come to the conclusion that the statement that cyanogen could be made to undergo luminous combustion has arisen from a yellow ammonia flame having been mistaken for one containing solid carbon; the author shows that by surrounding the cyanogen flame by nitric oxide, intense luminosity and a copious deposit of soot can be obtained.

The author contends that the flame is in reality divided into two zones—

1. The outer sheath of combustion,
2. The inner region of non-combustion,

and that the latter consists of an internal portion in which radiant heat is converting the hydrocarbons into acetylene; a luminous envelope which caps it, and in which more intense heat is decomposing the acetylene with emission of light, and the blue calyx at the bottom of the inner zone where the hydrocarbons are undergoing decomposition by water vapour and carbon dioxide without previous separation of carbon.

The author also contends that the incandescent carbon particles in the upper portion of the flame are acted upon by carbon dioxide and water vapour forming carbon monoxide and hydrogen, and that this action tends far more than combustion by the air to prevent their escape from the flame.

DISCUSSION.

Professor SMITHELLS said that he had always considered the acetylene theory ingenious, and feared indeed that its very attractiveness had led Professor Lewes to a one-sided and, in many cases, an erroneous interpretation of evidence. The question was not whether the explanation of luminosity afforded by the acetylene theory was conceivable, but whether the theory was really in harmony with ascertained facts; and this question, he still thought, was to be answered decidedly in the negative. As Professor Lewes had not read the whole paper, but had only drawn the attention of the meeting to certain points, he was unable to say to what extent Professor Lewes had dealt with the series of objections raised to the theory, and his remarks must not, therefore, be regarded as pretending to be a complete reply.

He wished that Professor Lewes would state explicitly what view he had as to the structure of an ordinary gas flame. Did he, or did he not, accept the old and generally accepted view, that the flame consisted of three distinct parts—a luminous region, a mantle, and a blue calyx at the base? Professor Lewes had attempted to define the parts of flame by reference to temperatures; and whereas at one time he indicated the mantle as the region of lowest temperature, he now appeared to agree that it was the hottest part. Did he still maintain temperature measurements to be a reasonable basis for defining the anatomy of the flame?

He did not consider that Professor Lewes had explained the extraordinary discrepancies that had been pointed out in his measurements of temperature; and he should like to know whether Professor Lewes had used the thermo-couple, as shown in the apparatus before them, or whether he had not, as implied in his previous papers, inserted the twist of the thermo-couple in a manner now admitted to be improper.

He still thought that it was misleading to speak of 80 per cent of the unsaturated hydrocarbons as being con-

verted into acetylene within the flame. If acetylene were the source of light, and if the light depended on the almost explosive character of its decomposition, there surely was some reason to ask for evidence that a mixture of gases containing 1·4 per cent of acetylene, 0·5 per cent of other unsaturated hydrocarbons, and 98 per cent of other gases (four-fifths of which were incombustible) could afford light in the manner stated. He considered that such a doctrine was incredible.

The evidence now adduced by Professor Lewes to show not that the acetylene flame was comparatively cool, but that, conceivably it might be so if the fact were not otherwise, was very remarkable. He could not exactly say what was the mechanical equivalent of light, but his recollection was that it was extremely small, and he advised Professor Lewes to look into what was known on this subject before committing himself to the view that the acetylene flame lost so large a fraction of its total energy in the form of light. However, this seemed to be a matter of little consequence, for there was no getting over the fact that the acetylene flame was surrounded by a mantle of extremely high temperature, and that a platinum wire introduced into it glowed at least as brightly as the carbon within the flame. That being the case, there was no occasion to explain that, hypothetically, the flame might be cool.

With regard to the cyanogen flame, he had nothing to withdraw from what he had said on a previous occasion, though he congratulated Professor Lewes on having now made a new and interesting observation. He had entirely failed to obtain evidence of carbon being separated in a cyanogen flame surrounded by burning hydrogen, and Professor Lewes had not shown that it was separated. The use of nitric oxide (which would in its luminous result remind them of the behaviour of that gas towards carbon disulphide) undoubtedly led to the separation of carbon, and supplied a piece of evidence which Professor Lewes was now entitled to claim.

Much circumstantial evidence, believed by Professor Lewes to favour the acetylene theory, had been adduced. Among it was a calculation which, having a striking practical aspect, might have considerable influence on some minds, and he desired to ask Professor Lewes to explain and justify it. It was intended to give the theoretical illuminating value of ethane, ethylene, and acetylene respectively, on the supposition that, in giving light after passing through the state of acetylene, they were resolved into carbon and hydrogen, and this calculation gave results in tolerable agreement with the illuminating value of the gases as determined by the photometer. The calculation was, he thought, unintelligible from a scientific point of view, but, even if the principle were admitted, seemed not only incorrectly made, but capable of affording a set of numbers entirely at variance with practical measurements, just as easily as numbers in harmony with them. He thought some explanation of this was due from Professor Lewes. He would only, in conclusion, say again, that his remarks must not be taken at all as his complete answer to Professor Lewes, whose manner of presenting his paper had rendered this impossible.

Professor RÜCKER thought that the use of a thermocouple in a flame above the melting-point of one of the metals was open to grave objection, on account of the uncertainty as to the temperature which the junction actually attained. The validity of Professor Lewes's experiment on the thermal value of the luminous radiation depended on whether the whole of the non-luminous radiation had been absorbed in the comparison experiment. This in turn depended in part on the dimensions of the apparatus. By the solution of a small quantity of an iron salt the absorptive power of the water would have been increased, while the light would not have been very largely diminished.

Professor THORPE remarked that a possible fallacy might underlie the deductions as to temperature drawn from the behaviour of a platinum wire in a flame con-

taining free carbon and carbonic oxide, on account of the specific chemical action which those substances might exert on the metal. The fact that a platinum wire would melt even in an ordinary candle-flame, which is not particularly hot, was known to Smithson Tennant, and is referred to by Davy, in his well-known paper. Davy also found that a filament of platinum could be fused by a flame of cyanogen in air, whereas the same wire was not melted by a hydrogen flame.

Mr. GROVES drew attention to Professor Lewes's statement, that the yellow light emitted by a jet of cyanogen when surrounded by a hydrogen flame was due to carbon liberated by the decomposition of the cyanogen, and suggested that if the image of the sun were thrown on to this flame by means of a lens, and the reflected light examined by methods familiar to physicists, it would be easy to ascertain whether the flame contained solid particles. In that case, not only would the light be found to be polarised, but, if examined spectroscopically, would exhibit the Fraunhofer lines. If the flame contained no solid particles, then the luminosity could not be due to liberated carbon; on the other hand, even if it were found to contain solid particles, it would not necessarily follow that these were carbon.

The PRESIDENT referred to a suggestion of Professor Lewes, that the great output of light from the acetylene flame may leave the flame itself comparatively cool. He thought that of the energy made kinetic by chemical changes within the flame, only a small part radiated out in waves of such a length as to be light. The small carbon particles in the flame lost much heat by radiation, and would thus be cooler than the non-radiating gases in which they floated. It was agreed that the outside of a flame was the hottest part. One of the causes of the splendour of the flame of pure acetylene was, no doubt, the high temperature to which the separation, as well as the oxidation, of the carbon and hydrogen contributed; but a suitable burner was necessary: the flame must have a large outer surface, and close within this must be spread, over the whole frontier, the little particles of carbon which glow for an instant and disappear.

Among the causes which make the flame of one gas brighter than that of another, might be a difference in the size and number of these solid particles. As one salt gave a large-grained and another a small-grained precipitate, so it might be with decomposing hydrocarbons; and as a given quantity of platinum wire coiled into a spiral, and held in a Bunsen flame, would give more light the smaller the gauge so the finer dust of carbon might make the brighter flame.

Some idea of the proportion between the surface of the flame and the actual surface of the glowing particles to which its light is due might be gained from a comparison with the filament of an electric glow-lamp. The radiating substance was similar in the two cases, and when the filament and current were such that the glow-lamp gave light of the same amount and colour as the gas-flame, it was likely that the glowing surfaces had a similar area.

Professor LEWES, in reply, said that he extremely regretted not having read his paper *in extenso*, as it contained answers to most of the objections advanced by Professor Smithells.

His views as to the structure of an ordinary gas-flame were that it contained four parts, but that three of these, namely, the non-luminous inner zone, the luminous sheath, and the blue calyx, were portions of the region in which no combustion, in the ordinary acceptance of the term, took place; whilst the outer mantle of the flame was the region of intense combustion, and is undoubtedly the hottest part of the flame. In a paper read in 1892, he had given a description of the structure of a gas-flame, but, in criticising this, Professor Smithells had evidently overlooked the fact that the portion of the paper following the description was devoted to an investigation as to the causes which led to the non-luminosity of hydro-

carbon flames, which showed that the outer envelope must be the hottest portion of the flame; but it is also manifest that the outer side of this mantle must be rapidly cooled by admixture with air and products of combustion, so that the maximum temperature will be near the inner side of this region, and it was the extreme outer portion of this zone which he had described in the words criticised by Professor Smithells.

He thoroughly agreed in condemning any temperature measurements of those portions of the flame in which active combustion was going on, but still believed in the measurements obtained in the area of non-combustion. Professor Smithells had pointed out that serious discrepancies existed between the temperatures recorded in a flat flame in the 1892 paper and in the 1895 paper, but as the one was from a No. 6 Bray, whilst the other was given by a 0000 Bray, it was difficult to understand on what grounds it could be expected that they would show any agreement, as the temperatures varied for every alteration in the size of the burner, and for every variation in the pressure at which the gas was burnt.

One of Professor Smithells' strongest points was that it was misleading to speak of 80 per cent of the unsaturated hydrocarbons being converted into acetylene within the flame—the statement he had made was that 80 per cent of the unsaturated hydrocarbons at the point just before luminosity commenced consisted of acetylene.

If a mixture of 1.5 per cent of acetylene and any gas which had a non-luminous flame was burnt, no luminosity would be generated, and no trace of acetylene would be detected at the top of the inner zone, it having been consumed before the temperature necessary for its decomposition was reached; but if 1.5 per cent of acetylene was led into the top of the inner zone of a flame of coal gas, from which the unsaturated hydrocarbons had been absorbed, then this addition would make the flame as luminous as if the unsaturated hydrocarbons had not been withdrawn, and he thought that Professor Smithells' doubt as to the truth of the acetylene theory was based largely on a misconception of this point.

As regards the experiments to show that a flame radiates a considerable amount of energy when emitting light, he was perfectly in accord with those who pointed out that the amount of energy converted into light was but small; there was also a large amount of heat radiated, and the experiment with the blackened bulb would give the total radiation cut off by the opaque coating, which when the flame was radiating freely would be lost to the flame. It would be preposterous to lay any great stress on this experiment, as the products of combustion were practically escaping uncooled.

He had made in a former paper a calculation to show that a ratio existed between the heat of formation of a hydrocarbon and its illuminating value, but he had been careful to point out that in our present absence of knowledge as to the heat relations existing at high temperatures, any such calculations were valueless except as showing that the greater the endothermic value of a compound the higher was its illuminating value.

Professor Smithells concludes that because a platinum wire held in the outer shield of a flame glows with the same incandescence as the carbon particles in the flame itself, therefore there is no need to assume any other source of heat than that given by the combustion going on in the flame walls.

He thought that this conclusion was based upon at least two fallacies. In the first place Professor Smithells had himself clearly pointed out that there is a temperature gradient on the horizontal plane in which there is an abrupt rise in temperature from the luminous sheath to the point of maximum combustion in the external envelope, and it therefore follows that the platinum wire held in the external envelope must be heated to a higher temperature than the carbon particles in the luminous sheath. Secondly, the conclusion is based upon the assumption that the emissive power for light of carbon and platinum

is the same, which is highly improbable. It has been shown that metals at high temperatures reflect light, and he thought it quite possible that some of the apparent brightness of the platinum wire might be due to light reflected from the luminous veil in front of which the wire was placed.

(To be continued).

NOTICES OF BOOKS.

Spectrum Analysis. ("Die Spectral Analyse"). By Dr. JOHN LANDAUER. Brunswick: Vieweg and Son. 1896. 8vo., pp. 174.

WE have here a most useful guide to spectroscopic analysis as applied in chemistry, physics, and astronomy. The author expresses his regret that this branch of scientific investigation, though it met with its origin in Germany, has not there met with the attention and general application which it so fully merits.

A history of spectroscopy is carried down from the first recognition of the yellow sodium flame by Thomas Melville, in 1752. His observations were followed up successively by John Herschel, Fox Talbot, W. A. Miller, and Swan, but the formal development of spectroscopy was reserved for Kirchhoff and Bunsen in 1859; their epoch-making memoir, "Chemical Analysis by Spectral Observations" ("Chemische Analyse durch Spectral Beobachtungen"), appeared in *Poggendorff's Annalen*, cx., 167. We next pass to the physical foundations of the methods, including the principles of the gratings as developed by Rutherford, and especially by Rowland. The spectroscopes of Kirchhoff and Bunsen, of Steinheil, of Browning, of Rutherford, and Thallon are figured and described. The direct-view spectroscopes of Amici, Janssen, and Browning and Christie are also represented; as also Sorby's micro-spectroscope. A modification of this last instrument is designed by Abbe and executed by Carl Zeiss, of Jena.

Particular notice is given—as it is fully due—to the spectrograph, a combination of the spectroscope with a photographic camera. Not the least important feature of solar and stellar spectroscopy is that it furnishes a convenient refutation of the erroneous dogma that the more general sciences, whilst they give aids to the more special disciplines, receive nothing in return.

As spectral auxiliaries, Dr. Landauer describes the appliances for obtaining flame spectra, spark spectra, the phenomena due to the silent discharge in Geissler tubes, as also the observation of the ultra-violet and ultra-red. There is a brief mention of Becquerel's phosphoroscope. We find no notice of the improved phosphoroscope of Crookes, and of its use in chemical research.

We come next to absorption-spectra, the source of light which they require, and the most convenient vessels for containing the solutions to be examined. For this purpose H. W. Vogel uses ordinary test-tubes. The arrangements for measurement and the scale are various; Bunsen places the yellow soda-line at 50, whilst Vogel fixes it at 0°.

The author distinguishes three kinds of spectra—the continuous, the fluted or grooved spectrum, and the line spectra. The influence of temperature and pressure are carefully considered. The cause of the origin of the Fraunhofer line is definitely shown. The influence of the state of aggregation, of the temperature of the solvent, &c., are next explained. Of the relations between the spectra of the different elements proposed by Lecoq de Boisbaudran, Ditte, Troost and Hautefeuille, Ciamician, Hartley, Grünwald, and Ames, those of the first and last mentioned authorities only seem to have maintained their position.

In the special part of the work we find the spectral characteristics of each element very fully laid down, as

far as the emission spectra are concerned. A similar treatment of the absorption spectra presents great difficulties, and has not yet been carried out.

Abney and Festing have not succeeded in detecting chlorine, bromine, and iodine in organic combinations.

In what may be called the astronomical portion of the work, we find, firstly, an account of the solar spectrum, as laid down in Rowland's table of wave-lengths. Many of the most important of the Fraunhofer lines are still not explained. The spectra of fixed stars of the third (least brilliant) class is conjectured to indicate the presence of a carbon compound (acetylene?).

In many respects this work is admirably calculated for the convenience of the student. Besides the table of contents, there is a double index, of the authors quoted and of the subjects. The biographical notes are very copious. A few only of the most recent books and memoirs have remained unnoticed.

To *savants* engaged with spectral research—would they were more numerous!—this book must be most strongly recommended.

CORRESPONDENCE.

ESTIMATION OF INSOLUBLE PHOSPHATE.

To the Editor of the Chemical News.

SIR,—With regard to the above and Mr. Allibon's letter (CHEMICAL NEWS, vol. lxxiii., p. 47), I can only say that with care very good results can be obtained with the modification I suggested of the uranium method.

I am quite aware of the disturbance caused by any considerable amount of iron and alumina, and if the manure contains much of these substances the process will not work; but in ordinary cases the quantity is very small, and works' chemists who analyse the materials will have some knowledge on this point.

I do not for a moment propose that the uranium method should supplant the usual gravimetric one; but there are times when works' managers require information without delay, and in such cases my proposal seems the only one available.

I may say my attention was first called to this matter by seeing the method mentioned in a text-book in use at the College of Science in Ireland.

As to the amount taken for analysis, 0.5 grm. is certainly small; but if the amount is large, and the "soluble" is also estimated by uranium, a low result will almost certainly be found, which is a more serious matter. A friend, whose ability and accuracy are beyond question, went into the whole matter in my laboratory, and clearly proved that if accurate results are desired it is unsafe to take more than about 0.5 grm. for the determination.

The uranium method still fills so much space in valuable text-books that I think I need make no apology for drawing further attention to it.—I am, &c.,

VINCENT EDWARDS,
Chemist to Messrs. Lawes & Co., Lim.

West End Pathological Laboratory,
55, Weymouth Street, Portland Place, W.

ON THE PRESENCE OF GOLD IN SILVER ORES.

To the Editor of the Chemical News.

SIR,—That small quantities of gold are to be found in many silver ores has been known for a long time; yet it constantly happens that the analytical chemist is only asked to determine the number of ounces of silver per ton of ore. Of course, the determination of the gold also makes the assay rather more expensive, but this slight economy is apt to prove "penny wise, pound foolish." It

is quite possible that the gold in some silver ores may have been overlooked for a long time. Here is a specimen of my own experience on this subject.

Many years ago I received from the late Sir James Anderson, of the Eastern Telegraph Co., a large batch of silver ore from the celebrated Comstock lode in California. The silver was present in various forms, but chiefly as sulphide, and as grey copper ore. I was requested simply to determine the amount of silver present, but I specially mentioned on the analysis sheet that the ore contained very appreciable quantities of gold also. To this intimation no attention appears to have been given. Many months afterwards, I took up one of the small fragments of rock not included in the powdered samples sent for assay. It was a compact felspathic rock of a light reddish brown colour, with thin streaks of what appeared to be sulphide of silver running through it, something like certain specimens of selenide of lead which I met with in the Hartz district. As it was evidently a rich specimen, I made an assay of it from pure curiosity, and, to my surprise, the button came out yellow instead of white; it contained much more gold than silver. A second assay, made with another fragment, also gave a yellow button, but lighter in colour and containing more silver. It would appear probable, therefore, that tellurium gold (sylvanite) accompanies the sulphide of silver (fahlerz, stephanite, &c.) in this rich Comstock lode, and has evidently been overlooked.

I may mention on this occasion that in olden times Vauquelin reported 1 to 10 per cent of platinum in some samples of fahlerz (grey copper ore), and F. Field found over 1 ounce of gold and 26½ ounces of silver in another sample of grey copper ore. If that quantity of gold could be extracted, it alone would more than pay the raising of the ton of ore, not to mention the copper and silver present. It is very probable that some of the Cornish grey copper ore may be found to yield gold also.—I am, &c.,

T. L. PHIPSON.

The Casa Mia Laboratory, Putney,
London, S.W., Feb. 1, 1896.

PREPARATION OF PURE ANHYDROUS HYDROCYANIC ACID.

To the Editor of the Chemical News.

SIR,—The following are original, easy, and direct methods of preparing pure anhydrous hydrocyanic acid:—

1. By the reaction of sulphuric acid, slightly diluted (to the strength of the ordinary brown oil of vitriol), or concentrated hydrochloric acid, on cyanide of sodium. In the first instance the reaction is so violent that the greater portion of the hydrocyanic acid passes over without the application of heat; but afterwards just sufficient will have to be applied to drive over the remainder of the acid.

2. By distilling cyanide of calcium with concentrated sulphuric or hydrochloric acid. As in the first process, the greater portion of the prussic acid passes over without heat being applied.

3. By passing dry arseniuretted hydrogen gas over perfectly dry potassium cyanide, gently heated in a glass tube connected with a small receiver cooled by a freezing mixture.

4. By distilling cyanide of lead with glacial acetic acid. There is another simple method which I have not yet tried, though it would doubtless succeed, viz., by distilling powdered Prussian blue (prussiate or ferrocyanide of iron) in hydrochloric acid gas.

I find that cyanide of arsenic, $\text{As}(\text{CN})_3$, which I discovered several years ago, is best obtained by the reaction of arsenious chloride on sodium or calcium cyanide; also by distilling cyanide of lead with arsenious chloride—or sulphide, perhaps.—I am, &c.,

G. W. BLYTHE.

Manor Cottage, Doddinghurst,
near Brentwood, Essex, February 1, 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 3, January 20, 1896.

Circulation of Air in the Soil.—P. P. Dehérain and M. Demoussy.—The experiments of the authors show the great advantage of liming strongly argillaceous soils. The lime, by hindering their clay from passing into suspension, preserves their porous structure, their reserves of moisture, and ensures the free circulation of the air. The action of lime is very different in different soils. If incorporated with a clay soil capable of breaking up under the action of prolonged rain, lime is useful, since it prevents the production of impermeability; but if, on the contrary, the soil resists water without breaking up, the addition of lime has in this respect no reason. We may thus tell the cultivators of strong soils that if, after heavy rains, they see water standing in their furrows, they should add lime or marl in order to secure the free circulation of air and moisture.

A Crookes's Tube of a Spherical Form showing the Reflection of the Kathode Rays by the Glass and the Metal.—Gaston Ségué.—A hollow sphere of glass in which a vacuum has been made to one-millionth of an atmosphere contains an electrode of aluminium in the shape of a star, placed at its centre. A second electrode has the form of a small disc, applied against the glass wall parallel to the star. If we introduce the apparatus in the circuit of an induction coil which yields sparks of 10 c.m., the disc being at the negative pole, we observe luminous phenomena which demonstrate the reflection of the kathode rays from the glass and the metal. The sheaf of kathode rays emitted strikes and illuminates the opposite wall; we see the black shadow of the star in the midst of the luminous spot. These same rays, being reflected on the glass, return to illuminate the glass wall, and form a second shadow of the star, larger than the first. Lastly, the aluminium star reflects a part of the sheaf. Hence there results a luminous projection of this star in the middle of the shadow of the same star formed on the wall. If we take the aluminium star as kathode, the luminous phenomena are simplified. We merely see the star projected on the glass walls opposite, giving two luminous images in their true size.

Solubility of Sodium Thiosulphate in Alcohol.—P. Parmentier.—The solubility of the three modifications of thiosulphate (hyposulphite), the ordinary, the modified, and the superfused, increases with the temperature and with the degree of dilution.

Iron Nitrososulphides.—C. Marie and R. Marquis.—The authors give to these compounds, called by their discoverer, Roussin, nitrosulphides, the name nitrososulphides. The crystals obtained are black; they are soluble in water, alcohol, and especially in ether, in chloroform, acetone, and acetic ether, but insoluble in benzene and ligroine. Their percentage composition is:—Iron, 38.64; sulphur, 15.50; nitrogen, 16.36; water, 6.62; oxygen (by difference), 22.88. These figures lead to the crude formula $\text{Fe}_3\text{S}_2\text{N}_5\text{O}_6 + \text{H}_2\text{O} \cdot 1.5$.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Chemically Pure CS_2 .—Having occasion to use some chemically pure, odourless CS_2 , I should be much obliged if any of your readers could give me the name of any firm from whom I could get some.—J. K. W.

MEETINGS FOR THE WEEK.

- MONDAY, Feb. 10th.—Society of Arts, 8. (Cantor Lectures). "Alternate Current Transformers," by Dr. J. A. Fleming, F.R.S.
Medical, 8.30.
- TUESDAY, 11th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.
Institute of Civil Engineers, 8.
Medical and Chirurgical, 8.30.
Photographic, 8. (Anniversary).
- WEDNESDAY, 12th.—Society of Arts, 8. "Water Purification by means of Iron," by Sir Douglas Galton, F.R.S.
Pharmaceutical, 8.30.
Sanitary Institute, 8. "Influence of Subsoil Water on Health," by S. Monckton Cope-
man, M.D.
- THURSDAY, 13th.—Royal, 4.30.
Royal Institution, 3. "Some Aspects of Modern Botany," by Prof. H. Marshall Ward, F.R.S.
Institute of Electrical Engineers, 8.
Mathematical, 8.
- FRIDAY, 14th.—Royal Institution, 9. "Fish Culture," by J. J. Armistead.
Astronomical, 3. (Anniversary).
Physical, 5. (Annual Meeting). "Determination of High Temperatures with the Meldometer," by W. Ramsay and N. Eumorfopoulos.
- SATURDAY, 15th.—Royal Institution, 3. "Realism and Idealism in Musical Art," by Prof. C. Hubert H. Parry, D.C.L., &c.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1890.

ON THE X RAYS.

PROF. RÖNTGEN'S great discovery leads, as it might have been expected, to no little discussion. No one, indeed, denies the existence of the phenomena observed, but on their origin and their nature there is as yet little accord. Prof. Slaby, of Charlottenburg, has failed in obtaining the rays with a Crookes's vacuum tube, but has succeeded in producing them with what we may call a home-made tube, in which the vacuum was equal to 0.002 m.m. of mercury. He has also obtained good photographs with "Lenard rays,"—i.e., kathode rays which have travelled outside the tube in which they had been produced.

Prof. Röntgen does not accept the hypotheses which identify the X rays with either the ultra-red, the visible, the ultra-violet rays (such as have been hitherto studied), or the Lenard rays, and he gives important marks of difference.

Perhaps the best way to ascertain the nature of the X rays will be to work with them.

A correspondent, whose name we are not at liberty at present to make known, raises the question whether Prof. Röntgen's X rays permeate distilled water in a different manner from water containing invisible impurities, or, in a word, can they serve as an auxiliary agent in the hygienic analysis of waters?

He also suggests the use of a vacuum tube consisting not of glass, but of aluminium.

PHOTOGRAPHY WITH DARK LIGHT.

By GUSTAVE LE BON.

THE recent publication of experiments in photography, with light of a cathodic origin, has induced me to make known—though they are as yet very incomplete—some of the experiments which I have been conducting for two years on photography, through bodies which are opaque to ordinary light. The two subjects are very different, though the results present some analogies.

The following experiments prove that ordinary light, or at least some of its radiations, traverses without difficulty the most opaque bodies. Opacity is a phenomenon existing merely for an eye like ours; if constructed a little differently it could easily see through walls.

In an ordinary positive photographic case we introduce a sensitive plate, and above it any photographic proof whatever; then we place above the proof, and in close contact with it, a plate of iron covering entirely the front of the case. We expose the plate, thus masked by the iron plate, to the light of a petroleum lamp for about three hours. An energetic and prolonged development of the sensitive plate pushed to a total blackening will give, by transference, an image of the proof, very pale but very distinct.

If we slightly modify the above experiment, we obtain images almost as strong as if no obstacle had been interposed between the light and the sensitive plate. Without any change in the above arrangement, let us place behind the sensitive plate a sheet of lead, of any thickness, and bend down its edges so as to cover slightly the sides of the iron plate. The sensitive plate and the proof are thus imprisoned in a sort of metal case, the front of which is formed of the plate of iron, whilst the back and the sides are formed by the plate of lead. After an ex-

posure of three hours to the petroleum lamp, we obtain on development a strong image.

What is the part played by the sheet of lead in the second experiment? Provisionally, I suppose that the contact of the two metals gives rise to very feeble thermoelectric currents, the action of which is added to that of the luminous radiations which have traversed the iron plate.

I hope in future to succeed in ascertaining the rôle of the various factors which may come into play in producing the above results. I hope to be able to determine the properties of light after its passage through opaque bodies. The action which might be exerted by heat or by light stored up on the proofs has been already entirely eliminated in my experiments.

Sunlight gives the same results as the light of petroleum, and does not seem to act much more energetically.

Cardboard and metals—especially iron and copper—are easily traversed by light. The passage of light through the most opaque bodies is merely a question of time.

If we repeat the above experiments in the photographic camera,—i.e., if we place a metal plate before the sensitive plate, and consequently between this latter and the object to be photographed,—we obtain in two hours, with the sun, on developing, an intense blackening of the sensitive plate, which proves the passage of the light through the opaque screen; but we obtain images only very exceptionally, and under conditions which I have not yet been able to determine.

I have given to these radiations of an unknown nature, which thus pass through opaque bodies, the name of *dark light*, on account of its invisibility to the eye. On considering the difference between the number of vibrations which produce the different forms of energy, such as electricity and light, we may suppose that there exist intermediate members corresponding to natural forces still unknown. These latter may be connected by insensible gradations with the forces which we know. The possible forms of energy may be infinite in number. *Dark light* perhaps represents one of these forces which we do not know.—*Comptes Rendus*, cxxii., p. 188.

Before making known the new results of my researches on dark light, I give some indications destined to facilitate the reproduction of these experiments.

As the rapidity of the action of commercial photographic plates varies in the proportion of 1:4, it is evident that if, in order to obtain an image, we require three hours of exposure with very rapid plates, then on making use of plates of a rapidity of four times less we should obtain no result. Nor do we obtain a result if we do not make use of a developing agent sufficiently energetic.

I have taken care to explain (see above) that I have eliminated two factors of error; the possible influence of heat and that of light stored up in the proofs. After having used several methods, one of the most simple being to cut the proof in two parts and employ these parts for comparative experiments, I finally adopted a procedure consisting in using only proofs which had remained for a day in darkness in contact with a sensitive plate without giving any veil on developing. If such proofs then give images after exposure behind metallic plates, such images can evidently be due only to the influence of the dark light. I use always, moreover, the same proofs. As they are not taken out of their cases except in the laboratory, they cannot receive any other light than that which has passed through the metal plates; that is to say, dark light.

As for heat, I have satisfied myself, by keeping sensitive plates in contact with the proofs at a dark heat of 50°, that we do not obtain any trace of an image.

I have only made use of petroleum lamps for the sake of having a constant light. Daylight gives better results, but its intensity is too variable to allow of comparative experiments.

It is by no means necessary for the opaque plates to be in contact with the proofs. We obtain the same results if we place the plates at a small distance, so as to isolate the sensitive plate and the proof from all metallic contact.

I have the honour of submitting to the Academy negatives obtained as I have just described, through metal plates of about 0.5 m.m. in thickness.

The first negative has been obtained through a plate of aluminium, a metal very transparent for the dark rays. The image is as strong as if it had been obtained by the ordinary procedures.

The second image has been obtained with a thick medal of aluminium, simply laid on the case with its sides protected with black paper. The transparency of aluminium for dark light is such that we obtain an image of the upper surface of the medal by an exposure of less than two hours. I must add that the medal did not press upon the sensitive plate, as it was separated from this latter by the glass plate of the case.

The third image has been obtained through a plate of brass $\frac{1}{10}$ m.m. in thickness. This metal is likewise very permeable to the dark rays. The image is very distinct, but incomplete, since it occupies only the central part of the negative.

The fourth image has been obtained through a plate of sheet iron. It is very pale, but quite distinct.

On account of certain technical difficulties, I have not completed the exact determination of the degree of relative permeability of opaque bodies for the dark rays. I can, however, indicate that aluminium and copper are the most transmissive. Iron is less permeable. Zinc, silver, and tin are very slightly permeable. Black paper, and especially pasteboard covered with black paper, are transmissive to an infinitely slight extent.

Black paper, the kind employed for wrapping up packages of photographic plates, is one of the substances least readily permeable by the dark rays, notwithstanding its slight thickness ($\frac{1}{100}$ of 1 m.m.). If we superimpose black paper upon cardboard (which is exactly the process for packing up photographic plates) the opacity for the dark rays is almost complete, of course for brief exposures.

It will be remarked that the rays of cathodic origin pass very easily through the dark paper, though the dark rays scarcely traverse them. This is not the only distinction between the dark rays and those of cathodic origin.

I am about to examine within what limits the dark rays obey the laws of refraction and the deviations which they undergo in a magnetic field. Some of the results obtained caused me to believe that the dark light is composed of radiations of a different nature.—*Comptes Rendus*, cxxii., p. 233.

OBSERVATIONS ON G. LE BON'S RECENT NOTES ON DARK LIGHT.

By G. H. NIEVENGLOWSKI.

I HAVE repeated Le Bon's experiment in darkness *without any source of light*. The result has been the same as that of Le Bon, which seems to indicate that the image developed on the sensitive plate is derived from the luminous energy stored up by the proof when taking positive proofs, energy which it has preserved and communicated to the sensitive plate.

With this fact we may associate the following, indicated for the first time by Laoureux, and which I have frequently had the opportunity to observe:—

A plate exposed in the camera and not developed, being fixed in contact with, or at a small distance from, another sensitive plate which has not undergone the action of light, we may detect an image on *both*, the second being the feeblest. These experiments, which do

not succeed with all plates, seem, as Eder has said with reference to those of Laoureux, to be due to a kind of phosphorescence of the gelatin.—*Comptes Rendus*, cxxii., p. 232.

NEW PROPERTIES OF THE X RAYS.

By L. BENOIST and D. HURMUZESOU.

IN view of the various hypotheses by which an explanation of the recent experiments on the X rays has been attempted, we have endeavoured to study the action of these rays outside of, and rather far from, the Crookes tube in which they are produced,—action upon electrified bodies withdrawn at once from every luminous action, and from all external electric action.

We have caused the rays of a Crookes tube, incited by a powerful coil, to act upon the gold leaves of an Hurmuzesou electroscope at the distance of about 20 c.m. from the tube, and alternately charged with positive and negative electricity.

In this electroscope the insulated conductive system is in the interior of a Faraday cylinder formed of a rectangular metal cage put in communication with the earth, and which is closed by two movable windows, the nature of which can be charged at will. The insulation obtained by a disc of dielectric which closes the tube admits of a perfect preservation of the charge for several months.

By successively substituting the window opposite to the Crookes tube for the plates specified below, we obtain the following results:—

The X rays immediately and completely discharge the electroscope, more rapidly if the charge is negative than if it is positive. This action is produced across plates of metal (aluminium), forming a perfect screen, as well from a luminous as from an electrical point of view. It is produced with very different degrees of rapidity, according to the nature and thickness of the bodies interposed. We have thus a new way of investigation applicable to the study of these rays, and enabling us to gain important indications as to their real nature.

This is the summary of our present experiments:—

The plate to be studied being put in its place, the electroscope charged to about a divergence of 40°, the keeping-tube replaced, and the Crookes tube set in activity, we have observed:—

1. Black paper (sixteen leaves interposed), the collapse of the gold leaves is immediate and complete in a few seconds; they do not rise again.
2. Plate of brass ($\frac{1}{10}$ m.m. in thickness), no change in the divergence of the gold leaves.
3. Plate of aluminium ($\frac{1}{10}$ m.m.), immediate fall, complete in a few seconds; same result with plates of aluminium up to 1 m.m. and even upwards, and the Crookes tube being removed to the distance of 30 c.m.; the complete collapse of the gold leaves scarcely requires a few seconds more.

We have carefully verified the electric value of the metal screen formed by the cage and the plate connected with the earth.

The substances easily traversed are silver in beaten leaves, leaves of paper steeped in metallic solutions, vulcanised fibre, gelatin, celluloid, ebonite, &c.

The substances not traversed, at least in the thicknesses employed, are brass, zinc, glass, and unglazed porcelain (3 m.m.).

We purpose developing the use of a method for the investigation of the X rays.—*Comptes Rendus*, cxxii., p. 235.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst., Sir James Crichton-Browne presiding. The following were elected Members:—Mrs. Montagu, Mr. Robert R. Tatlock, F.C.S., and Mr. Ernest Westlake.

ON SOME PHYSICAL PROPERTIES OF
ARGON AND HELIUM.*

By Lord RAYLEIGH, Sec. R.S.

Density of Argon.

In our original paper (Rayleigh and Ramsay, *Phil. Trans.*, clxxvi., A, pp. 221, 238, 1895) are described determinations by Prof. Ramsay, of the density of argon prepared with the aid of magnesium. The volume actually weighed was 163 c.c., and the adopted mean result was 19.941, referred to $O_2=16$. At that time a satisfactory conclusion as to the density of argon prepared by the oxygen method of Cavendish had not been reached, although a preliminary result (19.7) obtained from a mixture of argon and oxygen (*loc. cit.*, p. 221) went far to show that the densities of the gases prepared by the two methods were the same. In order further to test the identity of the gases, it was thought desirable to pursue the question of density; and I determined, as the event proved, somewhat rashly, to attempt large scale weighings of pure argon with the globe of 1800 c.c. capacity employed in former weighings of gases (*Roy. Soc. Proc.*, Feb., 1888; Feb., 1892; March, 1893) which could be obtained in quantity.

The accumulation of the 3 litres of argon, required for convenient working, involved the absorption of some 300 litres of nitrogen, or about 800 litres of the mixture with oxygen. This was effected at the Royal Institution with the apparatus already described (*Phil. Trans.*, l. c., p. 219), and which is capable of absorbing the mixture at the rate of about 7 litres per hour. The operations extended themselves over nearly three weeks, after which the residual gases amounting to about 10 litres, still containing oxygen with a considerable quantity of nitrogen, were removed to the country and transferred to a special apparatus where it could be prepared for weighing.

For this purpose the purifying vessel had to be arranged somewhat differently from that employed in the preliminary absorption of nitrogen. When the gas is withdrawn for weighing, the space left vacant must be filled up with liquid; and afterwards, when the gas is brought back for re-purification, the liquid must be removed. In order to effect this, the working vessel, Fig. 7 (*Phil. Trans.*, l. c., p. 218) communicates by means of a syphon with a 10-litre "aspirating bottle," the ends of the syphon being situated in both cases near the bottom of the liquid. In this way the alkaline solution may be made to pass backwards and forwards, in correspondence with the desired displacements of gas.

There is, however, one objection to this arrangement which requires to be met. If the reserve alkali in the aspirating bottle were allowed to come into contact with air, it would inevitably dissolve nitrogen, and this nitrogen would be partially liberated again in the working vessel, and so render impossible a complete elimination of that gas from the mixture of argon and oxygen. By means of two more aspirating bottles an atmosphere of oxygen was maintained in the first bottle, and the outermost bottle—connected with the second by a rubber hose—gave the necessary control over the pressure.

Five glass tubes in all were carried through the large rubber cork by which the neck of the working vessel was closed. Two of these convey the electrodes: one is the syphon for the supply of alkali, while the fourth and fifth are for the withdrawal and introduction of the gas, the former being bent up internally, so as to allow almost the whole of the gaseous contents to be removed. The fifth tube, by which the gas is returned, communicates with the fall-tube of the Töpler pump, provision being made for the overflow of mercury. In this way the gas, after weighing, could be returned to the working vessel at the same time that the globe was exhausted. It would be

tedious to describe in detail the minor arrangements. Advantage was frequently taken of the fact that oxygen could always be added with impunity, its presence in the working vessel being a necessity in any case.

When the nitrogen had been so far removed that it was thought desirable to execute a weighing, the gas on its way to the globe had to be freed from oxygen and moisture. The purifying tubes contained copper and copper oxide maintained at a red heat, caustic soda, and phosphoric anhydride. In all other respects the arrangements were as described in the memoir on the densities of the principal gases (*Roy. Soc. Proc.*, liii., p. 134, 1893), the weighing globe being filled at 0° , and at the pressure of the manometer gauge.

The process of purification with the means at my command proved to be extremely slow. The gas contained more nitrogen than had been expected, and the contraction went on from day to day until I almost despaired of reaching a conclusion. But at last the visible contraction ceased, and soon afterwards the yellow line of nitrogen disappeared from the spectrum of the jar discharge.* After a little more sparking, a satisfactory weighing was obtained on May 22, 1895; but, in attempting to repeat, a breakage occurred, by which a litre of air entered, and the whole process of purification had to be re-commenced. The object in view was to effect, if possible, a series of weighings with intermediate sparkings, so as to obtain evidence that the purification had really reached a limit. The second attempt was scarcely more successful, another accident occurring when two weighings only had been completed. Ultimately a series of four weighings were successfully executed, from which a satisfactory conclusion can be arrived at.

May 22	3.2710
June 4	3.2617
June 7	3.2727
June 13	3.2652
June 18	3.2750
June 25	3.2748
July 2	3.2741

The results here recorded are derived from the comparison of the weighings of the globe "full" with the mean of the preceding and following weighings "empty," and they are corrected for the errors of the weights and for the shrinkage of the globe when exhausted, as explained in former papers. In the last series, the experiment of June 13 gave a result already known to be too low. The gas was accordingly sparked for fourteen hours more. Between the weighings of June 18 and June 25 there were nine hours' sparking, and between those of June 25 and July 2 about eight hours' sparking. The mean of the last three, viz., 3.2746, is taken as the definitive result, and it is immediately comparable with 2.6276, the weight under similar circumstances of oxygen (*Roy. Soc. Proc.*, liii., p. 144, 1893). If we take $O_2=16$, we obtain for argon—

19.940,

in very close agreement with Professor Ramsay's result.

The conclusion from the spectroscopic evidence, that the gases isolated from the atmosphere by magnesium and by oxygen are essentially the same, is thus confirmed.

The Refractivity of Argon and Helium.

The refractivity of argon was next investigated, in the hope that it might throw some light upon the character of the gas. For this purpose absolute measurements were not required. It sufficed to compare the pressures necessary in two columns of air and argon of equal

* Jan. 29.—When the argon is nearly pure, the arc discharge (no jar connected) assumes a peculiar purplish colour, quite distinct from the greenish hue apparent while the oxidation of nitrogen is in progress, and from the sky-blue observed when the residue consists mainly of oxygen.

* A Paper read before the Royal Society, January 16th, 1896.

lengths, in order to balance the retardations undergone by light in traversing them.

The arrangement was a modification of one investigated by Fraunhofer, depending upon the interference of light transmitted through two parallel vertical slits placed in front of the object-glass of a telescope. If there be only one slit, and if the original source, either a distant point or a vertical line of light, be in focus, the field is of a certain width, due to "diffraction," and inversely as the width of the slit. If there be two equal parallel slits whose distance apart is a considerable multiple of the width of either, the field is traversed by bands of width inversely as the distance between the slits. If from any cause one of the portions of light be retarded relatively to the other, the bands are displaced in the usual manner,

in the horizontal direction only, for the spherical lenses of ordinary eyepieces. For many purposes a single lens suffices, but it must be of high power. In the measurements about to be described most of the magnifying was done by a lens of home manufacture. It consisted simply of a round rod, about $\frac{1}{8}$ in. (4 m.m.) in diameter, cut by Mr. Gordon from a piece of plate glass.* This could be used alone; but as at first it was thought necessary to have a web, serving as a fixed mark to which the bands could be referred, the rod was treated as the object-glass of a compound cylindrical microscope, the eyepiece being a commercial cylindrical lens of $1\frac{1}{4}$ in. (31 m.m.) focus. Both lenses were mounted on adjustable stands, so that the cylindrical axes could be made accurately vertical, or, rather, accurately parallel to the length of the original

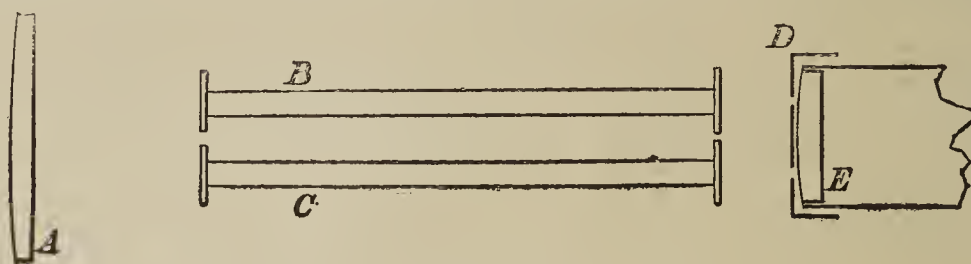


FIG. 1.

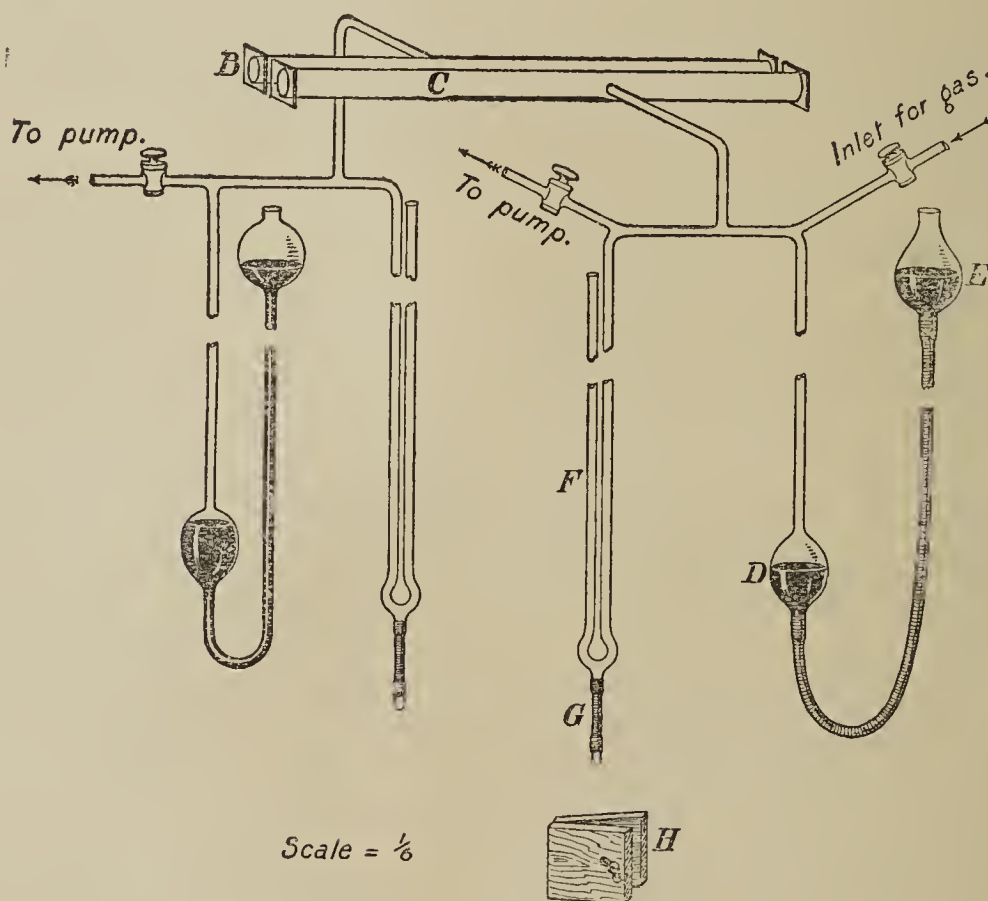


FIG. 2.

and can be brought back to the original position only by abolishing the relative retardation.

When the object is merely to see the interference bands in full perfection, the use of a telescope is not required. The function of the telescope is really to magnify the slit system (*Brit. Assoc. Report*, 1893, p. 703), and this is necessary when, as here, it is desired to operate separately upon the two portions of light. The apparatus is, however, extremely simple, the principal objection to it being the high magnifying power required, leading under ordinary arrangements to a great attenuation of light. I have found that this objection may be almost entirely overcome by the substitution of cylindrical lenses, magnifying

slit. The light from an ordinary paraffin lamp now sufficed, although the magnification was such as to allow the error of setting to be less than $1/20$ of a band interval. It is to be remembered that with this arrangement the various parts of the length of a band correspond, not to the various parts of the original slit, but rather to the various parts of the object-glass. This departure from the operation of a spherical eyepiece is an advantage, inasmuch as optical defects show themselves by deformation of the bands instead of by a more injurious en-

* Preliminary experiments had been made with ordinary glass cane and with tubes charged with water.

croachment upon the distinction between the dark and bright parts.

The collimating lens A (Fig. 1) is situated 23 feet (7 metres) from the source of light. B, C are the tubes, one containing dry air, the other the gas to be experimented upon. They are 1 ft. (30.5 c.m.) long, and of $\frac{1}{2}$ in. (1.3 c.m.) bore, and they are closed at the ends with small plates of parallel glass cut from the same strip. E is the object-glass of the telescope, about 3 in. (7.6 c.m.) in diameter. It is fitted with a cap, D, perforated by two parallel slits. Each slit is $\frac{1}{4}$ in. (6 m.m.) wide, and the distance between the middle lines of the slits is $1\frac{1}{2}$ in. (38 m.m.).

The arrangements for charging the tubes and varying the pressures of the gases are sketched in Fig. 2. A gas pipette, D E, communicates with the tube C, so that by motion of the reservoir E and consequent flow of mercury through the connecting hose, part of the gas may be transferred. The pressure was measured by a U-shaped manometer, F, containing mercury. This was fitted below with a short length of stout rubber tubing, G, to which was applied a squeezer, H. The object of this attachment was to cause a rise of mercury in both limbs immediately before a reading, and thus to avoid the capillary errors that would otherwise have entered. A similar pipette and manometer were connected with the air-tube B. In order to be able, if desired, to follow with the eye a particular band during the changes of pressure (effected by small steps and alternately in the two tubes), diminutive windlasses were provided by which the motions of the reservoirs (E) could be made smooth and slow. In this way all doubt was obviated as to the identity of a band; but after a little experience the precaution was found to be unnecessary.

The manner of experimenting will now be evident. By adjustment of pressures the centre of the middle band was brought to a definite position, determined by the web or otherwise, and the pressures were measured. Both pressures were then altered and adjusted until the band was brought back precisely to its original position. The ratio of the changes of pressure is the inverse ratio of the refractivities ($\mu - 1$) of the gases. The process may be repeated backwards and forwards any number of times, so as to eliminate in great degree errors of the settings and of the pressure readings.

During these observations a curious effect was noticed, made possible by the independent action of the parts of the object-glass situated at various levels, as already referred to. When the bands were stationary, they appeared straight, or nearly so, but when in motion, owing to changes of pressure, they became curved, even in passing the fiducial position, and always in such a manner that the ends led. The explanation is readily seen to depend upon the temporary changes of temperature which accompany compression or rarefaction. The full effect of a compression, for example, would not be attained until the gas had cooled back to its normal temperature, and this recovery of temperature would occur more quickly at the top and bottom, where the gas is in proximity to the metal, than in the central part of the tube.

The success of the measures evidently requires that there should be no apparent movement of the bands apart from real retardations in the tubes. As the apparatus was at first arranged, this condition was insufficiently satisfied. Although all the parts were carried upon the walls of the room, frequent and somewhat sudden displacements of the bands relatively to the web were seen to occur, probably in consequence of the use of wood in some of the supports. The observations could easily be arranged in such a manner that no systematic error could thence enter, but the agreement of individual measures was impaired. Subsequently a remedy was found in the use of a second system of bands, formed by light which passed just above the tubes, to which, instead of to the web, the movable bands were referred. The coincidence of the two systems could be observed with accuracy, and

was found to be maintained in spite of movements of both relatively to the web.

In the comparisons of argon and air (with nearly the same refractivities) the changes of pressure employed were about 8 in. (20 c.m.), being deductions from the atmospheric pressure. In one observation of July 26, the numbers, representing suctions in inches of mercury, stood—

Argon.	Air.
8.54	9.96
0.01	1.77
8.53	8.19

$$\text{Ratio} = 0.961,$$

signifying that 8.53 inches of argon balanced 8.19 inches of dry air. Four sets, during which the air and argon (from the globe as last filled for weighing) were changed, taken on July 17, 18, 19, 26, gave respectively for the final ratio 0.962, 0.961, 0.961, 0.960, or as the mean—

$$\frac{\text{Refractivity of argon}}{\text{Refractivity of air}} = 0.961.$$

The evidence from the refractivities, as well as from the weights, is very unfavourable to the view that argon is an allotropic form of nitrogen such as would be denoted by N₃.

The above measurements, having been made with lamp-light, refer to the most luminous region of the spectrum, say in the neighbourhood of D. But since no change in the appearance of the bands at the two settings could be detected, the inference is that the dispersions of the two gases are approximately the same, so that the above ratio would not be much changed, even if another part of the spectrum were chosen. It may be remarked that the displacement actually compensated in the above experiments amounted to about forty bands, each band corresponding to about $\frac{1}{2}$ in. (5 m.m.) pressure of mercury.

Similar comparisons have been made between air and helium. The latter gas, prepared by Professor Ramsay, was brought from London by Mr. W. Randall, who further gave valuable assistance in the manipulations. It appeared at once that the refractivity of helium was remarkably low, 13 in. pressure of the gas being balanced by less than 2 in. pressure of air. The ratios given by single comparisons on July 29 were 0.147, 0.146, 0.145, 0.146, mean 0.146; and on July 30 0.147, 0.147, 0.145, 0.145, mean 0.146. The observations were not made under ideal conditions, on account of the smallness of the changes of air pressure; but we may conclude that with considerable approximation—

$$\frac{\text{Refractivity of helium}}{\text{Refractivity of air}} = 0.146.$$

The lowest refractivity previously known is that of hydrogen, nearly 0.5 of that of air.

Viscosity of Argon and Helium.

The viscosity was investigated by the method of passage through capillary tubes. The approximate formula has been investigated by O. Meyer (*Pogg. Ann.*, cxxvii., p. 270, 1866), on the basis of Stokes's theory for incompressible fluids. If the driving pressure ($p_1 - p_2$) is not too great, the volume V_2 delivered in time t through a tube of radius R and length λ is given by—

$$V_2 = \pi t \frac{p_1^2 - p_2^2}{2p_2} \frac{R^4}{8\eta\lambda},$$

the volume being measured at the lower pressure p_2 , and η denoting the viscosity of the gas. In the comparison of different gases V_2 , p_1 , p_2 , R , λ may be the same, and then η is proportional to t .

In the apparatus employed two gas pipettes and manometers, somewhat similar to those shown in Fig. 2, were connected by a capillary tube of very small bore and

about 1 metre long. The volume V_2 was about 100 c.c., and was caused to pass by a pressure of a few c.m. of mercury, maintained as uniform as possible by means of the pipettes. There was a difficulty, almost inherent in the use of mercury, in securing the right pressures during the first few seconds of an experiment; but this was not of much importance as the whole time t amounted to several minutes. The apparatus was tested upon hydrogen, and was found to give the received numbers with sufficient accuracy. The results, referred to dry air, were for helium 0.96, and for argon 1.21, somewhat higher than for oxygen, which at present stands at the head of the list of the principal gases.

Gas from the Bath Springs.

In the original memoir upon argon (Rayleigh and Ramsay, *Phil. Trans.*, vol. clxxxvi., p. 227, 1895) results were given of weighings of the residue from the Bath gas after removal of oxygen, carbonic anhydride, and moisture, from which it appeared that the proportion of argon was only one-half of that contained in the residue, after similar treatment, from the atmosphere. After the discovery of helium by Professor Ramsay, the question presented itself as to whether this conclusion might not be disturbed by the presence in the Bath gas of helium, whose lightness would tend to compensate the extra density of argon.

An examination of the gas which had stood in my laboratory more than a year, having shown that it still contained no oxygen, it was thought worth while to remove the nitrogen so as to determine the proportion that would refuse oxidation. For this purpose 200 c.c. were worked up with oxygen until the volume, free from nitrogen, was reduced to 8 c.c. On treatment with pyrogallol and alkali, the residue measured 3.3 c.c., representing argon, and helium, if present. On sparking the residue at atmospheric pressure, and examining the spectrum, it was seen to be mainly that of argon, but with an unmistakable exhibition of D_3 . At atmospheric pressure this line appears very diffuse in a spectroscopic of rather high power, but the place was correct.

From another sample of residue from the Bath gas, vacuum tubes were charged by my son, Mr. R. J. Strutt, and some of them showed D_3 sharply defined and precisely coincident with the line of helium in a vacuum tube prepared by Professor Ramsay.

Although the presence of helium in the Bath gas is not doubtful, the quantity seems insufficient to explain the low density found in October, 1894. In order to reconcile that density with the proportion of residue ($3.3/200 = 0.0165$) found in the experiment just described, it would be necessary to suppose that the helium amounted to 25 per cent of the whole residue of argon and helium. Experiment, however, proved that a mixture of argon and helium, containing 10 per cent of the latter gas, showed D_3 more plainly than did the Bath residue. It is just possible that some of the helium was lost by diffusion during the long interval between the experiments whose results are combined in the above estimate.

Buxton Gas.

Gas from the Buxton springs, kindly collected for me by Mr. A. McDougall, was found to contain no appreciable oxygen. The argon amounted to about 2 per cent of the volume. When its spectrum was examined, the presence of D_3 was suspected, but the appearance was too feeble to allow of a definite statement being made. The proportion of helium is in any case very much lower than in the Bath gas.

Is Helium contained in the Atmosphere?

Apart from its independent interest, this question is important in connection with the density of atmospheric argon. Since the spectrum of this gas does not show the line D_3 , we may probably conclude that the proportion of helium is less than 3 per cent; so that there would be

less than 3×10^{-4} of helium in the atmosphere. The experiment about to be described was an attempt to carry the matter further, and is founded upon the observation by Professor Ramsay, that the solubility of helium in water is only 0.007, less than one-fifth of that which we found for argon (*Phil. Trans.*, vol. clxxxvi., p. 225, 1895).

It is evident that if a mixture of helium and argon be dissolved in water until there is only a small fraction remaining over, the proportion of helium will be much increased in the residue. Two experiments have been made, of which that on October 6, 1895, was the more elaborate. About 60 c.c. of argon were shaken for a long time with well boiled water contained in a large flask. When the absorption had ceased, the residue of 30 c.c. was sparked with a little oxygen until no nitrogen could be seen in the spectrum. It was then treated a second time with boiled water until its volume was reduced to $1\frac{1}{2}$ c.c. With this vacuum tubes were charged by my son at two different pressures. In none of them could D_3 be detected; nor was there any marked difference to be seen between the spectra of the washed and the unwashed argon. If helium be present in the atmosphere, it must be in very small quantity, probably much less than a ten-thousandth part.

ON THE OXIDATION OF SOME GASES WITH PALLADINISED COPPER OXIDE.*

By E. D. CAMPBELL.

(Concluded from p. 53).

In the case of easily burned gases, like hydrogen and carbon monoxide, it is not found necessary to re-oxidise the tube after each combustion, but in the case of more difficultly burned gases this was found desirable, especially when burning at the higher temperatures and when the previous combustion had removed a good deal of oxygen.

In the table all the quantitative combustions were performed with palladinised copper oxide, prepared by the first method, the ignition-point only of the various gases being determined with pure copper oxide in order to determine to what extent the presence of 1 per cent of palladium affected the temperature at which combustion commenced. In the calculation of the rate of combustion of ethylene and of propylene (experiments 18—25 and 28—34), the volume was calculated from the amount of carbon dioxide, since, owing to the use of phosphorus pentoxide in one arm of the U-tube used for collecting the water, there was slight polymerisation, which made the amount of water a little higher than the true value. On the other hand, in the case of isobutylene (experiments 37—41) the rate of combustion was calculated from the amount of water produced, the U-tube being filled with calcium chloride alone, thus avoiding polymerisation. The solubility of isobutylene rendered the carbon dioxide a little in excess of the amount calculated for perfect combustion, so that it was thought to be more accurate in this case to use the weight of water rather than that of carbon dioxide in calculating the rate of combustion.

In all of the gases on which quantitative combustions were made, although a slight excess of unburned gas was forced completely through the train, if the supply was slackened a little, perfect combustion took place and no unburned gas escaped. In the case of methane no combustion took place at 455° , and as 460° was the limit to which nitrogen-filled thermometers could be carried, it was found necessary to lay aside the work so far as the paraffins go until suitable modifications to the furnace can be made by means of which such temperatures as may be necessary for the combustion of these gases can be

* Contributions from the Laboratory of Analytical Chemistry of the University of Michigan. From the *American Chemical Journal*, vol. xvii., No. 9, November, 1895.

Exp. No.	Gas.	Initial combustion pt. with palladium copper oxide.	Initial combustion point with pure copper oxide.	Temp. of combustion. Deg.	Length of time in hrs.	Wt. H ₂ O.	Wt. CO ₂ .	C.c. of gas burned per hr.	Wt. O ₂ removed per hr.
1.	H ₂	80—85	—	—	—	—	—	—	—
2.	H ₂	—	175—180	—	—	—	—	—	—
3.	H ₂	—	—	115—120	6	0.4808	—	99	0.0713
4.	H ₂	—	—	125—130	6	1.295	—	266.4	0.1918
5.	H ₂	—	—	135—140	6	1.974	—	406.2	0.2925
6.	H ₂	—	—	145—150	6	3.544	—	729.2	0.525
7.	H ₂	—	—	165—170	6	3.688	—	754.8	0.5435
8.	CO	100—105	—	—	—	—	—	—	—
9.	CO	—	100—105	—	—	—	—	—	—
10.	CO	—	—	125—130	6	—	0.669	56.4	0.0406
11.	CO	—	—	135—140	6	—	1.0215	86.1	0.062
12.	CO	—	—	145—150	6	—	2.313	196.7	0.1403
13.	CO	—	—	155—160	2½	—	2.101	425.1	0.3059
14.	CO	—	—	175—180	1½	—	1.7685	599.5	0.4292
15.	CO	—	—	195—200	1½	—	1.951	654.9	0.4734
16.	C ₂ H ₄	240—250	—	—	—	—	—	—	—
17.	C ₂ H ₄	—	315—325	—	—	—	—	—	—
18.	C ₂ H ₄	—	—	270—275	2	0.0515	0.116	14.7	0.063
19.	C ₂ H ₄	—	—	295—300	2	0.111	0.268	33.8	0.145
20.	C ₂ H ₄	—	—	325—330	2	0.3215	0.815	103	0.442
21.	C ₂ H ₄	—	—	345—350	2	0.489	1.1725	148.5	0.636
22.	C ₂ H ₄	—	—	370—375	2	0.565	1.3665	172.8	0.741
23.	C ₂ H ₄	—	—	395—400	2	0.5985	1.4555	184	0.789
24.	C ₂ H ₄	—	—	420—425	2	0.742	1.830	231.4	0.993
25.	C ₂ H ₄	—	—	450—455	1½	0.561	1.388	234	1.004
26.	C ₃ H ₆	220—230	—	—	—	—	—	—	—
27.	C ₃ H ₆	—	270—280	—	—	—	—	—	—
28.	C ₃ H ₆	—	—	240—245	2	0.0315	0.0475	4	0.0257
29.	C ₃ H ₆	—	—	270—275	2	0.0905	0.179	15.1	0.0972
30.	C ₃ H ₆	—	—	295—300	2	0.2345	0.569	48	0.3089
31.	C ₃ H ₆	—	—	320—325	2	0.9505	2.332	196.5	1.265
32.	C ₃ H ₆	—	—	345—350	2	1.265	3.092	260.5	1.6695
33.	C ₃ H ₆	—	—	370—375	2	1.2505	3.0125	253.8	1.634
34.	C ₃ H ₆	—	—	395—400	2	1.271	3.0765	259.3	1.668
35.	iso. C ₄ H ₈	270—280	—	—	—	—	—	—	—
36.	C ₃ H ₈	—	320—330	—	—	—	—	—	—
37.	C ₄ H ₈	—	—	270—275	2	0.051	0.196	7.87	0.0755
38.	C ₄ H ₈	—	—	295—300	2	0.185	0.559	28.57	0.2454
39.	C ₄ H ₈	—	—	320—325	2	0.6765	1.8665	104.4	0.895
40.	C ₄ H ₈	—	—	340—345	2	1.6495	4.036	254.8	2.186
41.	C ₄ H ₈	—	—	370—375	½	1.431	3.4775	588.6	5.059
42.	CH ₄	No combustion at 455°.							

obtained and controlled, when the work will be continued. After obtaining the temperature of ignition and rate of combustion of the ordinary gases occurring in the pure state, mixtures of these gases will be worked upon in order to determine if possible to what extent they may be separated by fractional combustion. The combustion of acetylene differs from that of any of the gases given in the above table, since this gas does not burn at once to carbon dioxide and water, but undergoes a series of rather complex decompositions which would render it incapable of being separated by fractional combustion. In attempting to determine the ignition-point of acetylene, the pure dry grass was passed through a tube containing palladinised copper oxide, having a small tube of anhydrous cupric sulphate attached to the farther end, followed by a U-tube containing calcium hydroxide for the detection of carbon dioxide. A steady flow of gas was kept up through the tube, which was very slowly heated; no apparent change occurred until a temperature of 225°—230° was reached, when the first test for moisture was observed, but no carbon dioxide. The flow of gas was kept up, the temperature of the tube being gradually raised until a temperature of nearly 300° was reached, when the tube was found to be choked up although no test for carbon dioxide had as yet been obtained. On removing the combustion-tube from the furnace the palladinised copper oxide nearest the inlet of the tube was found to be filled for a distance of about 5 c.m. with

a heavy black deposit. The combustion-tube was re-filled with fresh palladinised copper oxide prepared by the second method, heated to nearly 300°, and acetylene once more turned through the tube and the temperature raised, when a test for carbon dioxide was obtained at 315°—320°. On removing the jacket from the furnace a deposit similar to the first was observed, but not in sufficient quantity to choke the tube; this deposit was removed by heating the tube to a red heat, and forcing in oxygen until everything was burned. After thus re-oxidising the tube the jacket was replaced and the temperature raised to and maintained at 345°. Acetylene was turned into the tube at such a rate that 3—5 bubbles per minute passed through the last bulb of the weighed potash bulb used for regular quantitative combustion. This was kept up for two hours, when it was found that the water obtained weighed 0.3171 grm. and the carbon dioxide 0.4834 grm. If combustion had been perfect to carbon dioxide and water, then the amount of water obtained should have been accompanied by 1.547 grms. carbon dioxide, instead of less than one-third this amount. On removing the jacket a deposit similar to the previous ones was observed, which was removed by oxidation at a red heat. A second quantitative combustion was then made, the temperature being 395°—400°. In this combustion the amount of water obtained was 0.4056 grm., accompanied by 1.4753 grms. carbon dioxide—a little greater ratio than the previous one. After removing the jacket the carbon-

aceous deposit was again removed by burning at a red heat, and the water and carbon dioxide produced were weighed. This gave: water, 0.0521 gm.; and carbon dioxide, 0.7737 gm. From these results we see that when acetylene is passed through a tube of palladised copper oxide at a temperature of 395° — 400° , two-thirds of the carbon and eight-ninths of the hydrogen are oxidised to carbon dioxide and water respectively, while one-third of the carbon and one-ninth of the hydrogen remain in the tube in a form as yet undetermined.

In a combustion similarly conducted, but with the temperature at 445° — 450° , the amount of water obtained in the same length of time was 0.6747 gm., accompanied by 1.9486 grms. of carbon dioxide, thus showing that while the rate at which dissociation took place increased with rise in temperature, oxidation did not seem to reach a higher limit than at 400° .

Credit is due Messrs. R. F. Flintermann, C. R. Rose, and E. B. Hart for the care with which they have carried out the laboratory work of the above research.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 68.)

I SHALL describe farther on the spectrum of the sulphate after it was dried under a bell-jar.

At least two-thirds of the sulphate of calcium, still damp, were gradually put into a large quantity of dilute sesqui-carbonate of ammonium, in a large covered platinum retort. These bodies were left together for twelve hours, taking care to shake the vessel which held them, from time to time. I then washed the carbonate by decantation. For the first five washings I used a very weak solution of sesqui-carbonate of ammonium, and finished with pure water. The washings were repeated so long as the water decanted, when filtered and evaporated down to nine-tenths of its volume, gave a precipitate with a barium solution. After the washing, the carbonate was put into a litre of water, through which was passed carbonic acid to saturation. The supernatant liquid, having settled, was decanted, and the carbonate was twice washed with pure water, then put again into 4 litres of pure water, through which was passed carbonic acid to saturation.

The clear supernatant liquid was gradually brought to boiling-point in a platinum retort, and replaced by an equal volume of pure water, through which carbonic acid was again passed. Eight litres of solution deposited about *six grms.* of granulated carbonate of calcium. Part of this precipitate, when put at once into a Bunsen flame, on a recently heated platinum-wire loop, did *not* colour it *at all*, and spectrum analysis of the flame only showed *very fleeting* traces of the sodium spectrum, and these were identical with those shown by the flame itself. The carbonate was dried under a bell-jar by sulphuric acid.

The bulk of the carbonate of calcium left in the large covered retort was dried in it on a water-bath, and sheltered from atmospheric dust.

To make carbonate from nitrate of calcium, free from strontium, obtained from arragonite and white marble, I proceeded just as I have described for nitrate from calc-spar, absolutely free from strontium. I can therefore dispense with going into details of this subject.

To resume:—

- A. As far as concerns the carbonate of calcium obtained from *Iceland spar*, I made it—
 - 1st. By decomposing the purified chloride yielded by the spar.
 - 2nd. By converting carbonate from chloride into nitrate, and by afterwards precipitating this nitrate by means of bicarbonate of ammonium.

- 3rd. By converting nitrate into oxalate, and reducing this into carbonate by the action of heat.

- 4th. By converting nitrate into sulphate, and afterwards transforming this sulphate into carbonate.

- 5th. By dissolving carbonate from sulphate in water charged with carbonic acid.

B. As regards carbonate of calcium made from *arragonite*, I made it by first transforming this compound into chloride free from iron, manganese, and silica, by precipitating the chloride by means of bicarbonate of ammonium, by dissolving the carbonate of calcium thus formed in nitric acid, and freeing the nitrate from the strontium in it, and finally re-precipitating the nitrate by bicarbonate of ammonium.

C. I made carbonate from *white marble* in exactly the same way that I have described for the carbonate from *arragonite*.

I converted into *chloride* a certain amount of oxide of calcium made by dissociating pure carbonate, obtained from marble. I took care to free this oxide beforehand from sodium, by heating it in an oxyhydrogen blowpipe. I effected this conversion both by heating the oxide to redness, in a current of dry hydrochloric acid, in a platinum boat inside a porcelain tube, and by melting the same oxide, mixed with a large excess of pure chloride of ammonium, in a platinum crucible, in an oxyhydrogen blowpipe.

A recently heated platinum-wire loop, when dipped into either of the melted chlorides thus made, and put into a Bunsen burner fed with coal-gas, or into a hydrogen flame, at once colours the flame yellow, and the colour due to calcium appears only after several moments. The sodium spectrum appears strongly until the chloride is almost entirely reduced to the form of oxychloride. Every attempt I have made to obtain chloride of calcium, which would not show the sodium line on spectrum analysis, failed absolutely.

When carrying on these researches, I had to bear in mind the strong tendency of chloride to combine with sodium. Having left some melted chloride of calcium, still in the boat or platinum crucible, under a glass bell-jar, carefully sheltered from atmospheric dust, it—by attracting the moisture of the air *very slowly* and *becoming liquid*—produced a solution which, when put into a Bunsen flame, gave it the colour due to sodium only, although, on spectrum analysis, I saw both the sodium and calcium spectra.

I have further noticed that, when leaving the solution of chloride in the air, under a bell-jar again, until it absorbed all the moisture it could from the air,—and this takes months to accomplish,—a time came when, on putting it into a Bunsen flame, the solid chloride itself gave it an intense yellow colour, and continued to give it this colour until the magnificent calcium spectrum, seen at the same time as the sodium line, had almost disappeared.

I repeated these experiments many times, and always with the same results. I have already mentioned that the same facts occur both with pure oxide of lithium when converted into chloride, and with chloride of lithium when left in air under a bell-jar.

Chlorides of calcium and lithium, by attracting moisture from the air, thus combine with sodium. I maintain that very hygroscopic bodies are similar to all surfaces the temperature of which is below dew-point, for they, by condensing moisture from the air on themselves, collect sodium at the same time. My study of water of condensation from air on to polished platinum, the results of which I have described in my "*Essai sur la Nature et la Quantité des Matières Minérales existant dans l'Air*," appears to me to render this explanation very feasible.

In any case, I do not think any chemist will be able to determine the weight of sodium combined thus with solid or liquid chloride of calcium, or say in what form the sodium exists in the chloride. And yet chloride of calcium which has been allowed to absorb moisture from the

atmosphere gives to flames the colour due to a sodium compound only.

These facts show how contrary to experience and reason it would be to attribute to a dissociation of the metal calcium or lithium, the presence of the sodium line shown by spectrum analysis in the cases mentioned.

Chemists will readily understand that I did not prepare all the products I have just mentioned at the same time. I will even say that they were prepared at very different times, modifying the methods as experience showed me fresh causes of error. These methods constitute the whole of my researches, and the means of reaching the end I had in view, which was to ascertain whether it was possible to obtain oxide of calcium of uniform composition, no matter what its origin.

I return to the characteristics of the different samples of carbonate of calcium, and the single sample of sulphate of calcium.

All these products, immediately after their production,—that is, whilst still moist, and above all before coming in contact with the air, to be dried,—when put into a Bunsen flame, gave it a *very transient* yellow colour, excepting the sulphate and the carbonate which was precipitated, by boiling, from the solution in water containing carbonic acid. In the oxyhydrogen blowpipe this colour disappeared almost at once, and was replaced by the colour due to calcium. The calcium spectrum appears *the same in all*, as it is described in the next chapter, *without a trace* of the sodium spectrum with the sulphate and the carbonate which was dissolved in water containing carbonic acid, and with *transient* traces of this spectrum with the other carbonates.

Without any exception, all the compounds of calcium which were dried in the platinum vessels in which they were made, or out of these vessels, but in contact with air, *free from dust*, instantly gave to flames the colour due to sodium, and showed the sodium spectrum until, by means of the oxyhydrogen blowpipe, all the sodium was eliminated.

The influence of the air is therefore of as much importance as that of the methods used to form these calcium compounds.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 16th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 70).

2. "The Action of Sodium Alcoholate on certain Aromatic Amides." By J. B. COHEN, Ph.D., and W. H. ARCHDEACON, B.Sc.

If acetanilide is dissolved in ether, and sodium methylate added, a crystalline addition compound of the formula $\text{Ph} \cdot \text{NH} \cdot \text{Ac}, \text{CH}_3 \cdot \text{ONa}$ is formed.

Similar compounds with sodium methylate and ethylate have been prepared from ortho- and para-acetoluide, α - and β -acetonaphthalide, benzanilide, and formanilide.

With formylphenylhydrazide, disodium formylphenylhydrazide is obtained. Benzamide yields a sodium compound of indefinite composition.

With propionanilide and butyranilide compounds similar to acetanilide sodium alcoholate appear to be formed in solution, but they could not be isolated. Sodium alcoholate does not react with diphenylacetamide and ethylacetanilide.

3. "Note on the Electrolytic Conductivity of Formanilide and Thioformanilide." By THOMAS EWAN, B.Sc., Ph.D.

The majority of the amides are too little soluble in

water to allow of measurements of electrolytic conductivity being made. Others, again, are decomposed by water too rapidly into acid and amine. The conductivity of formanilide shows that it possesses feebly acidic properties. In aqueous solution the sodium compound of formanilide is completely decomposed. In the case of thioformanilide, the sodium compound appears to exist in aqueous solution.

4. "The Action of Sugar on Ammoniacal Silver Nitrate." By J. HENDERSON, B.Sc.

The author has investigated the reducing powers of the following substances on ammoniacal silver nitrate, viz., glucose, lævulose, galactose, cane-sugar, starch, dextrin, lactose, and maltose. The results obtained may be thus summarised:—

1. When glucose, levulose, and galactose are heated with ammoniacal silver nitrate under the given conditions, a definite factor can be found in each case.

2. Cane-sugar, starch, and dextrin, when heated under the same conditions, exert no reducing action on ammoniacal silver nitrate.

3. In the case of lactose and maltose a definite factor cannot be obtained, owing to the gradual hydrolysis of the disaccharide by the ammonia.

5. "Solution and Diffusion of Certain Metals in Mercury." By W. J. HUMPHREYS.

The author has examined quantitatively the solution and diffusion of tin, lead, bismuth, zinc, copper, and silver in mercury with a view to determining the extent to which these phenomena differ, if at all, from the solution and diffusion of non-metallic solids in liquids. Pieces of metal were placed on the upper surface of a column of pure mercury, and samples of the liquid were taken at definite depths below the surface, and the amount of foreign metal estimated. As far as the experiments go, the author concludes that the solution and diffusion of metals in mercury do not essentially differ from those of non-metallic solids in liquids. Copper and silver dissolve in mercury to a very small extent at ordinary temperatures, but diffuse very rapidly.

6. "On some of the Ethereal Salts of Active and Inactive Monobenzoyl, Dibenzoyl, Diphenylacetyl, and Dipropionyl Glyceric Acids." By PERCY FRANKLAND, Ph.D., F.R.S., and JOHN MACGREGOR, M.A.

The following compounds have been prepared by the authors:—

Methyl dibenzoylglycerate (active). Long radiating needles melting at $58-59^\circ$.

$$\begin{aligned} [\alpha]_D \text{ at } 183^\circ &= +8.55^\circ; d_{183^\circ/4^\circ} = 1.0951. \\ \text{,, } 59.5^\circ &= +22.13^\circ; d_{59.5^\circ/4^\circ} = 1.1877. \\ \text{,, } 15^\circ \text{ (calculated)} &= +26.89^\circ. \end{aligned}$$

Methyl dibenzoylglycerate (inactive). Long radiating needles melting at 44.46° .

Ethyl dibenzoylglycerate (active). Radiating needles melting at 25° .

$$\begin{aligned} [\alpha]_D \text{ at } 183^\circ &= +8.62^\circ; d_{183^\circ/4^\circ} = 1.0599. \\ \text{,, } 16.5^\circ \text{ (superfusion)} &= +26.28^\circ; d_{16.5^\circ/4^\circ} = 1.1996. \\ \text{,, } 15^\circ \text{ (calculated)} &= +26.58^\circ. \end{aligned}$$

Propyldibenzoylglycerate (active). Liquid boiling at $267-269^\circ$ under 11 m.m. pressure.

$$\begin{aligned} [\alpha]_D \text{ at } 87^\circ &= +15.34^\circ; d_{87^\circ/4^\circ} = 1.1175. \\ \text{,, } 19.5^\circ &= +20.71^\circ; d_{19.5^\circ/4^\circ} = 1.1771. \\ \text{,, } 15^\circ \text{ (calculated)} &= +21.00^\circ. \end{aligned}$$

Methyl diphenylacetyl glycerate (active). Liquid boiling at $266-270^\circ$ under 17 m.m.

$$\begin{aligned} [\alpha]_D \text{ at } 77.5^\circ &= -14.10^\circ; d_{77.5^\circ/4^\circ} = 1.1427. \\ \text{,, } 14.5^\circ &= -16.06^\circ; d_{14.5^\circ/4^\circ} = 1.1972. \end{aligned}$$

Methyl monobenzoylglycerate (active). A dextro-rotatory liquid which, on distillation, yielded a more

dextro-rotatory distillate. It is probable that the original liquid consisted of the α - and β -isomeric monobenzoylglycerates, of which the α -compound would have the lower boiling-point, and that this α -compound is more dextro-rotatory than the β -compound.

Methyl monobenzoylglycerate (inactive). Crystallises in small warty groups melting at $92.5-93^\circ$. It is probable that this is the β -compound, the α -compound being liquid.

Ethyl monobenzoylglycerate (active). Radiating needles melting at 62° . This is probably the β -compound; it is lævorotatory, whilst the liquid from which it crystallised, and which would contain the α -compound, was dextro-rotatory. This solid ethyl monobenzoylglycerate is remarkable for its almost complete insensitiveness to temperature, thus—

$$[\alpha]_D \text{ at } 136.5^\circ = -9.47^\circ; d_{136.5/4^\circ} = 1.0886.$$

$$,, \quad 67^\circ = -9.80^\circ; d_{67/4^\circ} = 1.1547.$$

Methyl dipropionylglycerate (active). Liquid.

$$[\alpha]_D \text{ at } 15^\circ = -10.97^\circ; d_{15/4^\circ} = 1.1349.$$

The relationship between the rotatory power and the chemical constitution of these and other derivatives of glyceric acid is discussed, attention being again directed to the manner in which the rotation is more powerfully influenced by the qualitative character than by the mere mass of the groups attached to the asymmetric carbon atom. It is also pointed out that the reaction is more influenced by an element or group of elements introduced in the vicinity than by the same at a distance from the asymmetric carbon atom.

7. "On the Rotation of Optically Active Compounds in Organic Solvents. By PERCY FRANKLAND, Ph.D., F.R.S., and R. H. PICKARD, B.Sc.

The authors have investigated the variation in the value of $[\alpha]_D$ for methyl dibenzoylglycerate when dissolved in benzene, nitrobenzene, ethylene dibromide, and acetic acid respectively, employing a number of different concentrations in the case of each solvent. The molecular weight was also cryoscopically determined for a series of similar concentrations with each solvent.

The cryoscopic determinations showed that inactive methyl dibenzoylglycerate does not exist as a "racemised" molecule in these solvents, practically the same values for the molecular weight being obtained as with the active compound under the same conditions.

The cryoscopic values were, with all the concentrations employed, below the theoretical ones in benzene; in ethylene dibromide and nitrobenzene they were below the theory with dilute, and above the theory with strong solutions. In the case of acetic acid, the cryoscopic values were with all concentrations sometimes above, and sometimes below, the theoretical value.

The values of $[\alpha]_D$ in the benzene solutions were much in excess, whilst in the nitrobenzene and ethylene dibromide solutions they were much below the value for $[\alpha]_D$ exhibited by the pure substance; in acetic acid the values for $[\alpha]_D$ most closely approximated to that of the pure substance. Low cryoscopic values for the molecular weight of methyl dibenzoylglycerate were accompanied by high values for $[\alpha]_D$, and *vice versa*.

This relationship between $[\alpha]_D$ and indicated molecular weight is borne out by the behaviour of ethyl diacetyl-glycerate in benzene and acetic acid solutions respectively, only that in this case the low molecular weights and high specific rotations were obtained in acetic acid, the high molecular weights and low rotations in benzene solution.

The real value of $[\alpha]_D$ for an active body cannot be directly calculated from the rotation of its solution, even when the cryoscopic examination of that solution shows the molecular weight to be normal, and even a moderately accurate estimate of the real value of $[\alpha]_D$ can only be arrived at by the study of solutions giving normal molecular weights and extrapolating for infinite concentration on their rotation curves.

The explanation of these phenomena on the assumption of dissociation and association processes taking place in the several solutions, as has been suggested by Freundler, is discussed. The dissociation indicated by the low cryoscopic values obtained with methyl dibenzoylglycerate in benzene, and with ethyl diacetyl-glycerate in acetic acid solution, appears to be in harmony with the rotation phenomena only if the dissociation consists in the splitting off of the methyl and ethyl groups respectively, the active ion retaining in each case the acid radicles (benzoyl and acetyl). This conclusion is opposed to that arrived at by Freundler in the case of the diacidyl tartrates.

8. "Note on the Action of Hydrogen Chloride on Ethyl Alcohol." By J. C. CAIN, B.Sc., Ph.D.

The author refers to the statement recently made by Dr. Armstrong, in his presidential address to the Society, that "Perkin has established the incorrectness of the supposition that until recently has always been made, that hydrogen chloride, when dissolved in alcohol, acts fairly readily on it," and points out that this supposition has been known to be incorrect for a considerable time.

Berthelot, in 1880, found that no reaction takes place on making the solution, and Villiers found a reaction at $10-25^\circ$ only after some months. The author examined the action of hydrogen chloride on ethyl alcohol in 1893, and found that hydrogen chloride had no action on ethyl alcohol after acting for seventeen days at 0°C ., or for fifteen days at 15°C . The reaction probably begins at $20-25^\circ\text{C}$.

A saturated solution of hydrogen chloride in alcohol contains 39.06 per cent HCl, at 10°C . This is near the number found by Dr. W. H. Perkin, sen. (38.45 per cent). The temperature at which the experiment was made is not given, and was therefore probably higher than 10°C .

9. "Transformation of the Alkylammonium Cyanates into the corresponding Ureas." By J. WALKER and J. R. APPLEYARD.

A comparison has been made of the rates of transformation of the alkylammonium cyanates into ureas, and of the reverse transformation of the ureas into cyanates. In every case the results agree with the assumption that the cyanates are present in the aqueous solution in the form of two independent ions. In some instances the reverse transformation is well developed; for example, equilibrium is reached in a 1/15 normal solution of tertiary amyl ammonium cyanate when half of the cyanate has been transformed into tertiary amyl urea, no production of the urea beyond that amount taking place. No definite relation between the values of the constants and the nature and number of the replacing alkyl groups was observed.

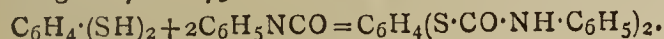
10. "On certain Phenylthiocarbamates." By H. LLOYD SNAPE, D.Sc., Ph.D.

The author has examined the action of phenylthiocarbimide upon phenol, resorcinol, quinol, and glycol. A. E. Dixon (*Trans.*, 57, 268) had already shown that interaction takes place between the above-named thiocarbimide and phenol; but his paper had been overlooked by the writer, who claims, in the course of the experiments he independently carried out, to have obtained the phenyl salt of phenylthiocarbamic acid in purer condition and in larger quantity. He found, in opposition to Dixon's experience, that the higher the temperature (below 280°) and the longer the duration of the experiment, the better was the yield, and in one experiment found this to amount to 25 per cent of the theoretical, whereas Dixon, working at lower temperatures and for a shorter time, only obtained 7 per cent. By crystallisation from absolute alcohol, the crystals obtained melted sharply at 148° ($149-151^\circ$, Dixon).

So much difficulty having been experienced in effecting combination between phenylthiocarbimide and phenol, it was to be anticipated that reaction between the former substance and dihydroxy-compounds would be even more difficult to carry out; and no thiocarbamate could be

obtained from resorcinol, quinol, or glycol. The writer, however, succeeded in obtaining, by the action of phenylcyanate upon dithioresorcinol and dithioquinol respectively, the isomerides of the thiocarbamates he had hoped to prepare by the foregoing method.

m-Phenylene Salt of Phenylenethiocarbamic Acid.—Phenylcyanate and dithioresorcinol, in the theoretical proportions, were heated in a bath containing a solution of common salt for half an hour. Crystals rapidly separated. After washing with cold alcohol and re-crystallisation from glacial acetic acid, large white needles were obtained, melting at 178° — 179° . The reaction is expressed thus—



p-Phenylene Salt of Phenylenethiocarbamic Acid.—Phenylcyanate and dithioquinol was heated in a water bath. Again combination readily occurred. The crystals obtained by re-crystallisation from glacial acetic acid were smaller than in the preceding case, and melted at 200° — 202° .

II. The Available Potash in Soils. By T. B. Wood M.A.

The author has had under his care a number of experimental plots in Norfolk and Suffolk, and in this paper he tests the practicability of Dr. Bernard Dyer's method of estimating available potash in soils (*Trans.*, 1894, 115—167), by comparing the analytical numbers obtained by Dr. Dyer's method with the results obtained in actual field experiment.

The soils experimented upon may be divided into two classes, viz., (1) those rich in available potash and (2) those poor in this substance. The former soils gave no marked crop increase (barley) when treated with potash manures, the latter gave a very large increase.

The former soils gave by Dr. Dyer's method on an average 0.0147 per cent of available potash (sol. in 1 per cent citric acid), the latter only 0.0073 per cent, whereas the potash soluble in strong hydrochloric acid (0.178 and 0.137) was much more nearly equal in each case.

The author concludes that Dr. Dyer's method is likely to be of technical value to the agriculturist; since, in the cases examined, laboratory experiments lead to the same conclusions as the more tedious and expensive field experiments. The modification of the method mentioned at the end of Dr. Dyer's paper for use in the case of soils containing much chalk gives far less satisfactory results than the unmodified analytical process.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 3, January 20, 1896.

Action of Carbonyl Chloride upon some Hydrogenous Compounds.—A. Besson.—The author has experimented on phosphonium bromide, phosphonium iodide, dry hydrogen phosphide, PH_3 , and hydrogen sulphide and selenide.

Dichloralglucose in Monochloralglucosane.—J. Meunier.—Dichloralglucosane, $\text{C}_6\text{H}_{16}\text{O}_4(\text{OC}_2\text{Cl}_3)_2$, crystallises in white needles insoluble in water, soluble in 300 parts of alcohol and 45 parts of ether at 20° . It is fusible at 225° , and resists the action of acids. Monochloralglucosane, $\text{C}_6\text{H}_9\text{O}_4(\text{OC}_2\text{Cl}_3)$, forms nacreous lamellæ, fusible at 225° , insoluble in water and cold alcohol, soluble in boiling alcohol, but re-deposited on cooling; soluble in 1000 parts of ether; not attacked by acids

Bulletin de la Société Chimique de Paris.

Series 3, Vols. xiii.-xiv., No. 15, 1895.

Researches on the Mercurous Salts.—Raoul Varet.—A thermochemical paper treating of the mercurous nitrate, sulphate, acetate, chloride, bromide, iodide, and oxide.

Alcohols derived from a Dextro-terebenthene: Eucalyptene.—G. Bouchardat and M. Tardy.

Isocampholic Acid.—M. Guerbet.—An account of the salts and the ethers of isocampholic acid.

Detection of Cotton Oil in American Lards.—J. Dupont.—The author points out that lards of American origin differ from European samples both as regards the indices of refraction taken with the oleo-refractometer, the iodine figure, and the action with silver nitrate.

Analysis of Lard and of similar Fats: Detection of Vegetable Oils.—Ferdinand Jean.—Vegetable oils, if added to lard, &c., increase the density, raise the iodine figure, lower the melting-point, the standard of fatty acids, Koerstorffer's number, and diminish the optical deviation. With the oleo-refractometer all the vegetable oils reflect to the right-hand of zero; hence lards mixed with vegetable oils show a deviation less than -12.5 , the normal deviation of pure lard. The animal fats change the density little, but lower the iodine figure, raise the melting-point and the standard of the fatty acids, increase Koerstorffer's number and the optical deviation of the oleorefractometer beyond -12.5° .

Revue Universelle des Mines et de la Metallurgie.

Series 3, Vol. xxxii., No. 2.

Congress on Building Materials.—In September last a Congress was held at Zurich to agree upon methods for the examination of building materials. The meeting seems to have confined itself simply to metals, though stone, cements, timber, paper, and protective coatings, each require separate study. A number of industrialists were present, from Germany, Austria, France, and Russia. Belgium, Britain, and America were scarcely represented. An International Association for the assay of building materials was organised; A Congress will be held at Stockholm in the course of 1897.

MEETINGS FOR THE WEEK.

MONDAY, 17th.—Society of Arts, 8. (Cantor Lectures). "Chemistry of certain Metals and their Compounds used in Building, and the Changes produced in them by Air, Moisture, and Noxious Gases, &c.," by Prof. J. M. Thomson, F.R.S.E.

Medical, 8.30.

TUESDAY, 18th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.

Society of Arts, 8. "The Development of Electrical

Traction Apparatus," by H. F. Parshall.

Institute of Civil Engineers, 8.

Pathological, 8.30.

Photographic, 8.

WEDNESDAY, 19th.—Society of Arts, 8. "Report of the Royal Commission on Secondary Education," by H. Macan.

Meteorological, 7.30.

Microscopical, 8.

THURSDAY, 20th.—Royal, 4.30.

Royal Society Club, 6.30.

Royal Institution, 3. "Some Aspects of Modern

Botany," by Prof. H. Marshall Ward, F.R.S.

Chemical, 8. "Origin of Colour—the Yellow 2-3-

Hydroxynaphthoic Acid;" "Note on Etherifica-

tion;" "The Relation of Pinene to Citrene;"

by Prof. Armstrong, F.R.S.

FRIDAY, 21st.—Royal Institution, 9. "The Past, Present, and Future Water Supply of London," by Dr. E. Frankland, F.R.S.

Quekett Club, 8. (Anniversary).

Geological, 3. (Anniversary).

SATURDAY, 22nd.—Royal Institution, 3. "Light," by Lord Rayleigh, F.R.S., &c.

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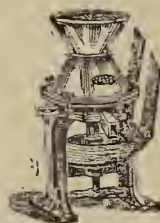
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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1891.

EXPERIMENTS WITH RÖNTGEN'S RAYS.

By ALBERT NODON.

THE voltaic arc produced in the air does not emit to an appreciable extent radiations having the property of traversing opaque substances like the rays of Röntgen.

A sensitive plate (silver gelatino-bromide) infolded in substances opaque to light,—*e. g.*, several thicknesses of black paper, and then exposed for fifteen minutes to the direct radiations of an arc of 20 ampères, at the distance of 0.40 metre, showed on development no sensible impression, whilst under the same circumstances it revealed a very distinct action of Röntgen's rays.

This result seems to demonstrate that the ultra-violet radiations of the spectrum in which the arc is rich do not appreciably traverse opaque substances.

Various coloured media are traversed by Röntgen's rays with equal ease. The experiment was made with a screen of leaf zinc perforated with apertures, before which there were arranged respectively plates of coloured gelatin, which transmitted only very limited portions of the spectrum. One of these apertures was kept open, and another was covered with uncoloured gelatin. After exposure to Röntgen's rays behind a screen of black paper, the photographic plate showed on development equal impressions produced through the various apertures.—*Comptes Rendus*, cxxii., p. 237.

PERMEABILITY OF METALS FOR THE X RAYS.

By V. CHABAUD.

I HAVE examined fourteen common metals or alloys as regards their permeability for the X rays. The results obtained are shown on the photographs which I have the honour of submitting to the Academy.

The metals examined have been rolled out to the thickness of 0.2 m.m., and cut up into rectangular slips 35 m.m. in length and 7 in width, and attached side by side, and in a parallel position, on one and the same cardboard. In addition a slip of platinum, of 1/100th m.m. in thickness, is superimposed as a check, intersecting the other slips transversely.

The sensitive photographic plate was protected against light by a double layer of black paper. The system of metal slips was laid against this paper during the exposure. The time of exposure was forty-five minutes, and the length of the sparks of the exciting coil was 7 c.m.

The metals thus compared were the following:—Lead, zinc, copper, zinc amalgam, tin, steel, gold, silver, aluminium, and platinum.

The experiment showed that, at the thickness of 0.2 m.m., platinum alone is perfectly opaque. Aluminium, as is already known, is very transparent.

The other metals above named are appreciably transparent.

Platinum itself, at the thickness of 1/100th m.m., is easily permeated, since the check band threw a slight shade upon the paper. This shade was seen traversing all those projected by the other metals, which shows their transparency.

Mercury deserves a special place. At the thickness of 0.1 m.m. it appears as opaque as platinum. In order to

obtain a plate of mercury of this thickness, I employed a trough hollowed in wood, 0.1 m.m. in depth, closed with a plate of varnished glass. It remains to be seen if—at the thickness, *e. g.*, of 1/100th m.m.—mercury in turn will appear transparent like platinum.—*Comptes Rendus*, cxxii., p. 237.

THE PHOTOGRAPHY OF METALLIC OBJECTS THROUGH OPAQUE SUBSTANCES, BY MEANS OF THE BRUSH OF AN INDUCTION-COIL WITHOUT A CROOKES TUBE.

By G. MOREAU.

ON repeating Röntgen's experiments on the photography of opaque objects by means of a Crookes tube, I have obtained, through a layer of cardboard of several metres in thickness, distinct proofs of different metallic objects (a steel key, the copper stand of a camera lucida, an aluminium wheel, &c.). All these proofs present the relief of the objects due to shadows, the orientation of which indicate that the active rays seem to come from the positive part of the Crookes tube.

I had the idea of substituting for the Crookes tube the brush of a strong induction-coil, actuated by a medium current of 6 ampères. The brush was produced between a positive point and a small negative plate on one or more negative points.

The sensitive plate was placed, along with the object to be photographed, in the interior of a box of cardboard, completely closed. The box could be placed normally or parallel to the effluve, and separated from it by cardboard, or a plate of wood 0.005 metre in thickness.

A first observation, made with five brushes normal to the box, gave nothing appreciable.

Six other photographs were taken with a parallel brush, and gave negative proofs, quite distinct and very intense.

All these proofs present a maximum of action at the level of the brush. They show thus that, as in the Crookes tube, the active rays come from the positive region of the oscillatory system.

The two photographs taken through wood indicate to me a notable absorption of the rays of a perceptible refraction, which I have not yet had the opportunity of measuring exactly.

The duration of the exposure varied from thirty to sixty minutes, and I hope to be able to reduce it in future, the intensity of the proofs indicating this possibility. I have tried to photograph the above objects with the brush of an electro-static machine. Hitherto I have obtained nothing.—*Comptes Rendus*, cxxii., p. 238.

A VIEW ON ARGON.

THE *Actualité Médicale*, a French medical paper, gives the following article, apparently from the pen of Dr. Foveau de Courmelles:—

Another product which I must be satisfied with mentioning, and the existence of which I had denounced (!) a glance of the mind, is a new body, produced, in my opinion, by atmospheric electricity: it is *ekazote*. Two English scientists have recently signalled the presence in the ambient air, not merely of oxygen and nitrogen, but of *ekazote*, which is for us electrified nitrogen, a companion to *ozone*, or electrified oxygen. In the inaugural lesson of my free course of electro-therapy, at the École Pratique de la Faculté de Médecine de Paris, I said, on April 24th, 1893, "Lightning furrows space, decomposes watery vapour, renders the *nitrogen electrified*, and then are formed *ozone*, ammonium nitrate, oxygenated water."

This, it will be said, was merely a glance of the mind, or hypothesis. Certainly so. But in Science do we not

commonly proceed by hypothesis and empiricism, the former of course preceding the latter. In the same manner as Leverrier signalled in space the presence of the planet Neptune, which was discovered two years afterwards by a Berlin astronomer.

The writer even suggests that De Romas and Franklin have probably anticipated Lord Rayleigh and Professor Ramsay in the discovery of argon, though without submitting any evidence for his opinion. He insinuates that Rayleigh and Ramsay have set out from the hypothesis—which they have formulated for themselves or heard formulated by some one else—that ozone, electrified oxygen, ought to have a pendant in the form of electrified nitrogen.

EXAMINATION OF WATER.

In testing the water of wells for possible contamination by the leakage of cesspools, &c., Nördlinger proposes to make use of saprol. This disinfective agent—which contains kresol—can be recognised by its odour, in the proportion of 1 : 1,000,000, and even in dilutions of 1 : 2,000,000 is betrayed by its characteristic taste. We should therefore have to pour saprol into cesspools which are suspected of infecting adjacent wells, and to examine the water of the latter as to its taste and smell.

A colorimetric determination of phosphoric acid in water, available up to a proportion of at most 5 m.grms. phosphoric acid per litre, is performed by Alessandri with the solution of molybdenum. He uses for comparison a solution of 0.1 grm. calcium phosphate in a few drops of nitric acid, which he first makes up to 1 litre, and then dilutes further as may be required. Waters containing a higher proportion of phosphoric acid must be suitably diluted, as otherwise the result is not a mere yellow colouration, but a precipitate. Silica must of course be previously eliminated.

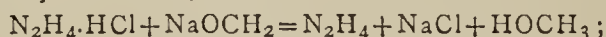
The author mentions a special case in which a high proportion of phosphoric acid does not justify the condemnation of a water, *i.e.*, when it is derived from the fossil remains of primeval animals. Phosphoric acid may be separated from water by ebullition as a calcium salt.—*Zeitsch. f. Analyt. Chem., and Pharm. Central-Halle.*

ON FREE HYDRAZIN.

By C. A. LOBRY DE BRUYN.

HYDRAZIN has been known hitherto only as hydrate (N_2H_6O) and in the form of salts. The hydrate is a liquid which has the constant boiling-point 119° . Its discoverer, Prof. Curtius, has in his latest memoirs expressed the conjecture that the free base is too unstable to exist in the free condition.

The free base may be obtained by two methods: by decomposing the hydrochlorate with sodium methylate in a methylic solution,—



or, secondly, by heating the hydrate with barium oxide to 100° and distilling under reduced pressure.

The following is excerpted from communications published elsewhere (*Ann. d. Chem.*, ccliii., 5, and *Berichte*, xxi., 1810):—Free hydrazin is a liquid boiling without decomposition at 113.5° (761 m.m.). On cooling below zero it solidifies, but melts at $+1.4^\circ$. Its specific gravity is about equal to that of the hydrate, *i.e.*, 1.003 at 23° . It is a very stable substance, and, unlike hydroxylamine and hydrogen peroxide, it is non-explosive. It may be heated without decomposition to above 300° .

With the halogens there is a very violent reaction. With solid sulphur it generates hydrogen sulphide even at common temperatures. Its sharply reductive power is

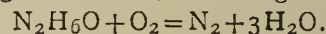
therefore manifested on contact with this element, since, like hydrogen iodide, it gives off its hydrogen to sulphur even at ordinary temperature. It is oxidised by oxygen with liberation of nitrogen, so that the free base cannot be exposed to the air. With sodium it sets up a violent reaction. The base dissolves various salts.—*Berichte*, No. 19.

ON THE PRODUCTION OF CERTAIN OF THE PROPERTIES OF HYDRAZIN HYDRATE.

By C. A. LOBRY DE BRUYN.

ELSEWHERE I have shown that hydrazin hydrate can be conveniently prepared without a special apparatus of silver if the distillation and fractionation are effected at a reduced pressure. If we reduce the temperature to 50° the glass is not attacked. We proceed by distilling off chiefly large quantities of a solution obtained from sulphate and potassa in a tinned copper still (the distillate being fractionated if necessary), an approximately equal quantity of alcohol added to the residue, the potassium sulphate filtered off, and the alcohol is first distilled off from the residue at the ordinary pressure. Dilute solution of hydrate is then added until the temperature has risen to 115° , and the hydrate is, lastly, fractionated at a pressure of 100–150 m.m. We thus obtain a very good yield.

At the pressure of 26 m.m. the hydrate boils at 47° . It is not decomposed on boiling for seven hours. On exposure to the air it is readily oxidised, with a formation of nitrogen. By oxygen it is decomposed quantitatively without a change of volume, according to the equation—



It readily dissolves several salts, *e.g.*, potassium bromide, iodide, and cyanide, ammonium sulphate, barium nitrate, magnesium sulphate, potassa, soda, and gaseous ammonia, but sodium chloride, potassium and lead nitrates less readily.

Sulphur reacts readily with the hydrate, hence vulcanite is easily attacked by the vapours and the liquid. A brownish red liquid is produced containing sulphur and ammonium sulphide in solution.

White phosphorus gradually takes a yellow reddish violet and black colouration, and a faint odour of hydrogen phosphide is perceptible. On dilution with water a black precipitate is deposited, probably a solid hydrogen phosphide. Sodium reacts rather violently with the hydrate. These reactions agree with those of free hydrazin.—*Berichte*, No. 19, January 19, p. 3086.

ON THE YELLOW AUTUMNAL COLOURING-MATTER OF LEAVES.

By G. STAATS.

It seemed to me interesting to decide whether in the autumnal colouration of leaves the chlorophyll is split up into the two components phylloxanthin and phyllocyanin, and in such a manner that the latter is destroyed whilst the phylloxanthin occasions the yellow colouration of leaves.

On digesting in boiling alcohol the thoroughly yellow leaves of the summer linden (*Tilia euchlora*), we obtain an intensely yellow solution. In order to compare this solution with that of phylloxanthin I decomposed the chlorophyll of the lime-tree and the acacia (*Robinia*) into phylloxanthin and phyllocyanin by the introduction of hydrochloric acid vapours according to Schunck's method. I thus obtained much more phyllocyanin from the chlorophyll of the acacia than from that of the linden. The phylloxanthin from the leaves of both trees showed the red fluorescence of chlorophyll, whilst this phenomenon did not appear in the alcoholic extract of the linden

leaves which had turned yellow in autumn. Hence the autumnal yellow (or, as I propose to call it, autumnixanthin) is not identical with phyloxanthin.

In the boiling, alcoholic solutions of the autumnixanthin of the linden and the hornbeam solution of potassa produced reddish-brown precipitates and yellow solutions. The precipitates are insoluble in ether and alcohol, but soluble in water. Hydrochloric acid dissolves them with a yellow colour. But if we add the solutions of autumnixanthin drop by drop to a little boiling hydrochloric acid, and concentrate as far as possible at a boiling temperature, continuing the addition of the autumnixanthin, we obtain red solutions, which in the case of the linden leaves are of the colour of port wine. The precipitate obtained with potassa lye in a boiling extract of the autumnixanthin of the linden dissolves in water with a splendid garnet-red colour, but it is obtainable only from the solution of large quantities of purely yellow freshly fallen linden leaves. Leaves which have been lying upon the ground for some time, or have been discoloured by frost, yield little red pigment. Such a decrease is not observed with hornbeam leaves. The red potassium compound obtained from the autumnixanthin of the linden crystallises from alcoholic water (at the temperature of a dwelling room) in fine reddish yellow needles, often a m.m. in length. The pigment of beech-autumnixanthin obtained by the same reaction is likewise crystalline.

The splendid red alcoholic extract of the autumnal leaves of the "blood-oak" (*Quercus ruber*) gives the same reaction with potassa lye. On adding the potassa lye the red solution first turns to a chlorophyll-green, and then becomes yellow with the separation of a reddish-brown precipitate, which, as in the above-mentioned reactions, is insoluble in alcohol and ether, but dissolves in water with a reddish-yellow colour.

The precipitates obtained with potassa-lye are soluble in hydrochloric acid when the yellow colour returns.

The potassium reaction seems therefore to take place identically for the pigments of the various leaves as modified by the autumnal change, and forms an appendage to the scission of chlorophyll by alkalis as observed by E. Schunck.

Whether the yellow pigment formed in the autumnal change, which I obtained only in an amorphous state (though some of its compounds crystallise), pre-exists in the green leaves I did not succeed in deciding. In the alcoholic extracts I examined only the compounds of the chlorophyll, or the decoctions of the leaves of the linden, the ash, the beech, and the oak, yielded reddish-yellow solutions, containing tannin. In the reaction-products of autumnixanthin I could not detect any tannin.

Being induced by the experiments of Timiriazoff, I experimented on the discolouration of the kinds of chlorophyll in the living cell. Nascent hydrogen, acetic acid, and sulphuric acid acted with equal strength on both kinds of chlorophyll. Direct sunlight bleached the acacia chlorophyll—generally very stable—in the living cell with the formation of a flocculent precipitate.—*Berichte*, No. 17, p. 2807.

VOLUMETRIC DETERMINATION OF CHLORO-PLATINATES, DETERMINATION OF POTASSIUM, AMMONIUM, NITROGEN, OR PLATINUM.

IN order to determine the potassium volumetrically with a solution of silver the potassium compound in question is first converted into a chloride. This is effected by precipitating the potassium as a platinum double salt, collecting it, igniting it along with a reducing agent, and extracting the residue with water. F. Mohr remarks concerning this process, that as regards the accuracy of the process it would be advantageous to determine the total chlorine of the platinum double salt. He therefore reduces the

double salt by ignition with sodium oxalate, and extracts the residue with water. L. L. de Koninck proposes to dissolve the double platinum salt in boiling water, and to reduce it with magnesium ribbon. This process, however, still leaves something to be desired in point of accuracy, whence he has subsequently effected the reduction with magnesium in the form of powder, and thus obtains accurate results. Determinations of this method are, however, rendered more difficult by the fact that the magnesium of commerce almost always contains chlorine.

De Koninck further attempted (*Chemiker Zeitung*) to reduce the double platinum salts by formiates, a procedure which had been previously proposed by Corenwinder and Contamine (*Comptes Rendus*). The chloroplatinate, obtained in the usual way, is collected on a filter, washed in alcohol, and dissolved in boiling water or formiate free from chlorine formiate. The author used calcium formiate, which is easily purified by re-crystallisation. The mixture is then heated for some time until the platinum is totally deposited, and the supernatant liquid is perfectly colourless.

The solution is neutralised by the addition of a trace of calcium carbonate, the platinum is filtered off, washed with hot water, and the chlorine is determined in the filtrate in the known manner.

The author has proved the practicability of this process by experiments with pure potassium platinochloride.

The process is applicable without any modification to the determination of ammonia and of nitrogen, if the latter can be converted quantitatively into ammonia. Platinum can also be determined in this manner after it has been separated out as a platinum double salt, or in combination with organic bases. In the organic platinum double salts the total chlorine and the platinum can be determined by this method in one portion.

The reduction of the platinum salts by formiates can also serve for the elimination of platinum in the separation of potassium and sodium. In this case we use ammonium formiate, which is produced in the solution by adding first a little formic acid and then ammonia, until the reaction is slightly alkaline.—*Zeit. für Analyt. Chemie*.

NOTE ON THE BROMINE HEAT-VALUE OF OILS AND FATS.

By J. A. WILSON.

IN a recent number of the *Analyst* (July, 1895, p. 146), Messrs. Hehner and Mitchell describe a new thermal method for the examination of oils and fats which, briefly described, is as follows:—

1 grm. of the sample is dissolved in 10 c.c. of chloroform in a vacuum-jacketted test-tube, 1 c.c. of bromine is added, and the rise of temperature noted. In default of a vacuum-jacketted test-tube, an ordinary test-tube packed in cotton-wool may be employed. The above observers find that the latter plan gives results two degrees lower than the use of a vacuum-jacketted test-tube; but this, of course, will depend on the total rise of temperature being greatest, say, with linseed oil, and lowest with oils such as cocoanut and palm-nut oils. I find, however, that up to a rise of 17° C. the observed rise of temperature $\times 1$ gives very nearly the iodine value. I ought previously to have mentioned that Hehner and Mitchell find that the observed rise of temperature multiplied by the factor 5.5 gives very nearly the Hübl or iodine value.

I have made some determinations on oils and fats which sometimes come under my notice and, in the main, agree with the authors of the process as to accuracy and convenience. I find that in the case of cocoanut oil, which gives a very low thermal value, that the factor $\times 5.5$ gives at once almost the correct iodine value. With tallow, lard, and butter the observed rise of temperature

in a test-tube packed in cotton-wool requires the addition of 1 before being multiplied by the factor 5.5.

The following table corroborates the above remarks:—

Name of oil or fat.	Rise of temp. with bromine.	Calculated iodine value.	Observed iodine value.
Cocoanut oil	1.5	8.2	8.4
S. A. tallow	7.0	43.2	44.0
Olive oil (pure) . .	14.0	82.5	82.0
Rape oil	18.0	104.5	103.4

THE ANALYSIS OF TIN SLAG.

By HENRY BAILEY, F.C.S.

THE slag obtained in the smelting of tin ores, and which is technically known as "glass slag," to distinguish it from the particles of unburnt culm locally known as slag, consists principally of double silicate of alumina and iron, containing a variable amount of stannous silicate, minute shots of metal, and in rare cases unreduced stannic oxide, together with small quantities of lime, tungsten, &c.

For technical purposes a knowledge of the amounts of iron, tin, and silica present is usually required, and the following scheme has been devised for their rapid determination.

The principal difficulty experienced in the opening up of tin slag is to obtain the silica in a granular, easily filtered condition, at the same time obtaining all the tin in solution. The ordinary method of decomposing silicates by fusion with alkaline carbonates, with subsequent evaporation with hydrochloric acid, is inapplicable, owing to the volatility of tin chloride during the evaporation to complete dryness.

Two grms. of the slag, reduced to the finest possible state of division in an agate mortar, are placed in an evaporating dish with 10 c.c. red fuming nitric acid, and evaporated to complete dryness on a sand-bath, the heating being continued until brown fumes cease to be evolved.

The nitric acid decomposes the silicates, rendering the silica granular, at the same time converting all the tin present into insoluble oxide. Twenty c.c. of strong hydrochloric acid are then added, and boiled for some time: this can now be done, as, the tin being insoluble, there is no danger of loss as chloride.

When all soluble matter has dissolved, dilute with an equal bulk of water, and place two sticks of zinc—each about an inch long—in the solution, and allow to stand until the iron is all reduced to the ferrous state, and all action ceases. It is best to allow the assay to stand in a warm place for about an hour, to ensure complete reduction of the tin.

Remove the rods of zinc, carefully scraping off and washing back any adhering spongy tin; filter and wash: titrate the iron in the filtrate with standard bichromate of potassium. Wash the spongy tin and silica from the filter-paper back into the dish, add 10 c.c. strong hydrochloric acid and a few drops of nitric acid (just enough nitric acid to oxidise the tungsten), and warm until the silica appears white; dilute, filter, and wash the silica well with boiling water.

Through the warm filtrate pass a rapid current of sulphuretted hydrogen, and allow to stand in a warm place until the sulphide of tin has completely settled and the odour of SH_2 nearly dissipated; filter, wash, dry, carefully ignite, and weigh the stannic oxide. Wash the silica with dilute ammonia, and finally with water; dry, ignite, and weigh.

An approximate idea of the amount of tungsten present in the slag may be obtained by evaporating and igniting the ammoniacal washings from the silica in a weighed platinum dish, and weighing the residual tungstic acid.

When it is desired to determine the alumina present in

the slag, the solution containing the iron and alumina, instead of being titrated direct, is nearly neutralised with carbonate of soda, 10 grms. of sodic hyposulphite added, and boiled until the odour of SO_2 has disappeared. The mixed precipitates of oxide of alumina and sulphur are filtered off, washed, dried, ignited, and weighed. The filtrate, containing the iron, is acidified with an excess of hydrochloric acid, boiled until free from SO_2 , and titrated with standard bichromate.

ON THE CASTING OF STEEL.

By SERGIUS KERN, M.E. St. Petersburg.

At the Obouchoff Steel Works, St. Petersburg, great inconvenience was felt for a long time in casting large round ingots of 5 tons and upwards, for forging guns. The stream of steel falling from a considerable height into the mould, from the 30-ton ladles of the Siemens-Martin furnaces, gives rise to a considerable quantity of splashes, which in return produce cracks on the surface of the ingots.

The same annoyance was also observed in casting rectangular ingots of 25 to 30 tons for armour plates.

M. Posnikoff, the manager of the steel department of the above-named works, has devised a very simple method, preventing the steel from splashing. It may perhaps be already in use elsewhere, but anyhow it deserves mention.

A tube is prepared of thin sheet-iron, such as is used for roofing. The tube is 24 inches in inside diameter, and is suspended from an iron ring, to which there are rivetted three bars on the surface of the mould just before casting. The steel is poured from the bottom of the ladle into the middle of the iron tube. All the splashes are thrown on the walls of the tube, which gradually melts away during the rise of the surface of the liquid steel in the mould.

We had the pleasure of seeing this device in perfectly successful action at the Obouchoff Works, where it is now in constant use.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 81.)

CHAPTER VI.

ON THE CHARACTER IMPARTED TO FLAMES, AND TO AN ELECTRIC SPARK, DISCHARGE, AND ARC, BY THE SALTS OF CALCIUM.

The Luminous Spectra of Calcium.—I made some researches on the character imparted to flames, and to the electric spark, discharge, and arc, by the salts of calcium, for the purpose of finding out whether the luminous spectra of calcium, barium, and strontium had any common relation among themselves and with the luminous spectra of sodium, potassium, and lithium. I obtained some carbonate of calcium from several sources, to see if anhydrous calcic-oxide made from it was always the same, and whether this oxide could be brought to such a state of purity that, when volatilised in an oxyhydrogen blowpipe at the fusing-point of iridium, spectrum analysis would not show the sodium spectrum, assuming that the air does not supply any sodium.

For this purpose I used colourless and transparent Iceland spar, arragonite, white marble, prepared oxalate and sulphate, and carbonate which had been dissolved in water charged with carbonic acid.

In the preceding chapter I described the method of ob-

taining carbonate of calcium, of uniform composition, free from all foreign bodies except traces of sodium, and capable of being reduced, by means of a properly regulated temperature and a current of gas, to the form of pure oxide of calcium.

It is generally stated that anhydrous calcic-oxide is greyish; what I obtained was quite *white*, even after being kept for some time at the fusing-point of iridium. This oxide gives a *deep red* colour to that part of an oxyhydrogen flame whose temperature is high enough to melt platinum, and a *deep reddish brown* or chocolate-brown colour to the part which is nearly as hot as melting iridium. The colour is *sky-blue* at the temperature of *melted* iridium.

In my opinion, the *red flame tipped with yellow*, generally attributed to calcium, is due to the presence of sodium in the compounds experimented on. For the sodium line is visible in all calcium flames coloured red with a *yellow point*, and when the sodium line disappears the flame is coloured deep red, brownish red, or sky-blue, according to the temperature.

I did not see the sodium line in the luminous spectrum of calcium flames, when, just before making a spectrum analysis, I had taken the precaution of keeping the oxide of calcium for a sufficient length of time at the fusing-point of platinum, and when the carbonate used to make the oxide had been most carefully protected from *atmospheric dust*. The experiment gave no trouble, and the result was conclusive. It was always successful, provided that oxide of calcium *absolutely free from silica* was used; for this body, in the presence of oxide of calcium, retains sodium to such an extent that it is extremely difficult to eliminate it, even at the fusing-point of iridium.

So-called pure Iceland spar and arragonite contain from 1/7000th to 1/8000th of their weight of silica, and minute traces of sodium; nevertheless, when they are put on to the top of a cone of pure oxide of calcium on a sheet of platinum, and heated in an oxyhydrogen blowpipe, they colour the flame *red with a yellow point*, and show a very brilliant sodium spectrum. I have not carried the experiment through to the end, but, after my numerous failures, I am fully convinced that the sodium line will be visible until all the oxide of calcium derived from the spar or arragonite has been volatilised.

Oxide of calcium is more volatile than it is usually thought to be; it vaporises at the freezing-point of platinum, and at the fusing-point of iridium it is volatilised with such rapidity by an oxyhydrogen or oxy-coal-gas blowpipe, that the air becomes pungent for breathing.

The Spectrum of Calcium in an Oxyhydrogen Blowpipe.—Having described these facts, I will give the results of the spectrum analysis of a flame, as seen alternately by M. Rommelaere and myself, in the different conditions of our work.

Carbonate of calcium, looked upon as pure, but which had been for some time in contact with air, *under a bell-jar, the edge of which was ground, polished, and greased, and stood on a smooth sheet of glass*, was put into a conical cup on a recently heated sheet of platinum. I eliminated the carbonic acid and sodium absorbed from the air, by means of an oxyhydrogen blowpipe with an excess of hydrogen. This could be effectually done without volatilising much oxide of calcium.

Spectrum analysis of that part of the jet which impinged on the calcium salt showed at first a very strong sodium and a very weak calcium spectrum.

On passing the blowpipe jet over the surface of the calcium oxide,—renewed by means of a recently-heated platinum spatula,—the sodium spectrum decreases and the calcium spectrum increases in brightness. When the experiment is carefully done, all traces of the sodium line disappear before the appearance of the blue line in the spectrum of chlorine in hydrogen, at 135 micrometer divisions on the Bunsen spectroscope. *Having thus quite eliminated it, the oxide of calcium can be raised to the*

highest possible temperature, without causing the sodium line to reappear.

To make certain of the accuracy of this observation, I made experiments on every point. I heated the oxide of calcium in a conical cup, successively in oxyhydrogen with an excess of hydrogen, and with the exact proportion for the production of water, taking care each time to project on to the point of the oxide of calcium cone, resting on the sheet of pure iridium, that part of the flame where one obtains the maximum temperature—that of the fusing-point of iridium. *I was absolutely unable to cause the appearance of the sodium line.* Thus these observations left no doubt in my mind.

I found the spectrum of oxide of calcium to consist of bands and lines, or of ill-defined lines entirely, according to the temperature and the analyser used. The bands were only seen before the blue line appeared; after this blue line appeared, if the slit were sufficiently narrow, the bands became simplified,—they were better defined, and divided up into *ill-defined* lines.

The appearance of the bands did not seem to me to occur in the order of refrangibility. I first saw the second red band, then the nebulous green line, then the yellow and orange-yellow bands, and lastly the blue line.

Although they appeared in this order, when well above the fusing-point of platinum, yet, when using a sufficiently narrow slit, with hydrogen not brought to incandescence, the spectrum of pure oxide of calcium in an oxyhydrogen flame consists of a dark back-ground, marked by well-defined bands and lines, mentioned by M. Bunsen, in his "Spectral Analytische Untersuchungen," as occurring with chloride of calcium in a *hydrogen flame*.

The details of the calcium spectrum, both bands and broad lines, are so permanent that it is impossible to doubt that they are characteristic.

When I heated the *top* of a cone of pure oxide of calcium in an oxyhydrogen blowpipe, fed with two parts of hydrogen to one of oxygen, by volume,—which makes the *shortest but hottest* flame,—and took care to project the upper third of the inner cone of the blowpipe on to the oxide, the whole of the calcium spectrum became luminous, and a *pale violet-blue band* with hazy edges, situated between 148 and 149 micrometer divisions on my spectroscope (from 161.4 to 161.5 on that of M. Bunsen) appeared. This band appeared to consist of *at least two lines* very close together; it was very transient; at the slightest movement of the blowpipe, forward or backward, it became invisible. I was more successful in seeing the double blue line when subjecting to an oxy-coal-gas blowpipe some oxide of calcium formed by decomposing a cone made of a mixture of nitrate and oxide.* This oxide is very granular and is not displaced by the blowpipe flame so easily as anhydrous calcic oxide made from carbonate. The displacement of the latter oxide is inconvenient, because it admits of being easily reached by the blowpipe without being entirely volatilised. The incandescent solid then shows a continuous spectrum, which partially masks bands and lines of the calcium spectrum.

My observations of the double pale blue line in the flame spectrum of calcium date from the end of December, 1878. Having had occasion, during the summer of 1879, in collaboration with my late friend H. Sainte-Claire Deville, to melt *eighty-five grms.* of pure iridium in a lime crucible containing pure oxide of calcium, made by myself (an operation which is not difficult when metal containing a few thousandths of platinum is used, but

* To prepare a cone of *granular* oxide of calcium, I dissolved hydrate of calcium, without sodium, in a 10 per cent solution of nitric acid, distilled in platinum: after rapidly evaporating the solution down until it would solidify on cooling, I added enough hydrate of calcium, without sodium, to enable me to mould it into a cone. I immediately put this cone on a sheet of *pure iridium*, which had been previously heated to decompose the basic nitrate of calcium, and without delay I turned a coal-gas and air blowpipe on to it; and finally, I projected the inner cone of the shortest and hottest oxyhydrogen blowpipe flame on to the top of the cone.

which is extremely difficult with iridium entirely free from foreign bodies), we found, during the whole time we kept the metal melted in an oxy-coal-gas blowpipe, a *very strong* second blue line. Notwithstanding that there was an abundance of free oxide of calcium in the air throughout, we did not see the deep red calcium vapour; the gas inside the crucible was *sky-blue*. We saw exactly the same thing in an *oxyhydrogen blowpipe*. In addition to this, Messrs. H. Sainte-Claire Deville and Debray had, during their previous work, occasion to notice that the gas inside a lime crucible, when raised to the highest temperature attainable by a powerful blowpipe fed with oxygen and coal-gas, is coloured not *red*, but *blue*.

In order to see the double blue line, it is necessary to place the spectroscopie as near as possible to the mouth of the furnace, taking care to arrange it obliquely, and especially outside the current of gas.

The Stability of the Combination of Sodium from the Air with Oxide of Calcium.—When left under a large bell-jar in air free from dust, oxide of calcium does not give the slightest indication of the presence of sodium; on heating it in air in an oxyhydrogen or oxy-coal-gas blowpipe, to a temperature at which the calcium spectrum is no longer visible, it colours the blowpipe flame pure yellow. Still, the sodium spectrum thus shown is very fugitive; it very soon disappears entirely with a sufficient rise of temperature, and reappears no more.

On the Flame Spectrum of Sulphate of Calcium.—Sulphate of calcium, made as described in the previous chapter, gave just the same spectrum as oxide of calcium in an oxyhydrogen or oxy-coal-gas blowpipe. This identity occurs throughout the time the sulphate is being fused, and persists after it is entirely dissociated, until enough oxide of calcium has been freed to render the remainder infusible. It is difficult to do this experiment in platinum, because the temperature of dissociation is the same as the fusing-point of platinum, this latter being attacked by the heated sulphate; but it succeeds beautifully when an oxyhydrogen or oxy-coal-gas blowpipe is projected on to a cone of spongy iridium on a concave sheet of platinum entirely covered with fused sulphate of calcium, or on to a cone of sulphate on a bed of pure iridium. When using the products of dissociation of sulphate, I saw the double blue calcium line, above mentioned, on a very bright back-ground; the products of dissociation were so evenly distributed that it was very easy to make observations.

(To be continued).

ON THE VOLUMETRIC DETERMINATION OF LEAD.

By ALLERTON S. CUSHMAN and
J. HAYES-CAMPBELL.

FRESENIUS, in the last edition of his "Quantitative Analysis," commenting on the volumetric determination of lead, says:—"Although there is no lack of proposed methods for the volumetric estimation of lead, we are still without a really good method for practical purposes, that is, a method which can be generally employed, and which is simple and exact."

Among the methods which have been proposed, one which has been so much used is that of Schwartz (*Dingl. Poly. Jour.*, clxix., 284), briefly outlined. This depends upon precipitating the lead as chromate in a sodium acetate solution with a standard solution of potassium bichromate, the end point being determined by an outside indicator consisting of drops of a neutral solution of silver nitrate on a porcelain plate. It is exceedingly difficult to decide when the first red tinge makes its appearance in the indicator, owing to the yellow colour of the precipitated lead chromate. The end point is therefore frequently overrun. W. Diehle (*Zeitschr. Anal. Chem.*,

1880, 306) modified the method by titrating the excess of bichromate in acid solution with sodium thiosulphate, the end point being indicated by the disappearance of the yellow colour of the bichromate. In our experience this modification does not lessen the difficulty of determining accurately the end point, owing to the fact that the yellow colour gradually shades off into a green in case a fair excess of bichromate has been added.

These considerations led us to endeavour to modify the original method in such a manner as to secure a simple and accurate means of determining the excess of bichromate present. This we accomplish by titrating the solution after filtering off the precipitated lead chromate, with a standardised solution of ammonio-ferrous sulphate, using potassium ferri-cyanide as an outside indicator, under exactly the same conditions observed in standardising bichromate solutions. The bichromate solution is made up of convenient empirical strength, and standardised against a weighed amount of pure dried ammonio-ferrous sulphate. Slightly more than the equivalent weight of the latter salt is then weighed out and dissolved in a litre of water, with the addition of a few drops of sulphuric acid. The solution is transferred to a stock bottle, into which is immediately poured a sufficient quantity of some light paraffin oil to form a layer over the solution, thus protecting it from oxidation. The stock bottle is fitted with a syphon tube and pinchcock, so that the solution can be drawn out when needed. With this arrangement change in strength of the ammonio-ferrous sulphate solution takes place very slowly, while, as a few moments only are required to titrate it against the standard bichromate, its exact strength can be easily determined from day to day.

In order to test this modification, we decided to try it against other technical methods recently proposed, as well as against a standard gravimetric analysis. A well-mixed sample of a crystallised galena, containing only a little silica as impurity, was first analysed by the method of Rose as given in Fresenius's "Quantitative Analysis." The lead is precipitated as the sulphide, with the proper precautions; the sulphide is then dried, ignited gently in a current of hydrogen, and weighed. The following results were obtained:—

No.	Weight taken. Grms.	Weight lead sulphide. Grms.	Lead sulphide. Per cent.	Lead. Per cent.
1	2.0000	1.9870	99.35	86.08
2	2.0000	1.9856	99.28	86.00
3	1.9988	1.9856	99.35	86.06

The next series of results were obtained by the method of Albert H. Low (*Journ. Anal. Appl. Chem.*, vi., 12). Briefly, the method consists in decomposing the ore with nitric and sulphuric acids, adding further an excess of sulphuric acid, dissolving the lead sulphate in a saturated solution of ammonium chloride, and precipitating metallic lead by means of strips of aluminum. The precipitated lead sponge is scraped off, pressed into a button, dried, and weighed. By this method the following results were obtained:—

No.	Weight taken. Grm.	Weight lead. Grm.	Lead. Per cent.
1	0.5000	0.4341	86.82
2	0.5013	0.4311	86.00
3	0.4972	0.4313	86.64
4	0.5025	0.4371	86.98
5	0.5019	0.4351	86.25
6	0.5223	0.4540	86.92

These figures show a general tendency to high results, which is accounted for by the difficulty of washing the lead sponge free from ammonium chloride. In view of the fact, however, that one of these assays can be made in about twenty-five minutes, the results might be considered fair enough for some technical purposes.

The next method tried was Knight's (*Journ. Anal. Appl. Chem.*, vi., 11) modification of Hempel's method. This consists essentially in the precipitation of the lead as oxalate, the decomposition of this salt by means of sulphuric acid and titration of the liberated oxalic acid, with potassium permanganate. This method did not yield concordant results in our hands, and the percentages found were invariably low. As the method did not present any advantage over others, either in points of accuracy or time, we discontinued work with it.

The modified Schwartz method we carry out as follows:—About 1 gram. of finely-pulverised ore is digested in a casserole or evaporating dish with 15 c.c. of a mixture of two parts nitric acid and one part sulphuric acid, until decomposition is complete. Ten c.c. more of sulphuric acid are now added, and the liquid evaporated until it fumes freely. Cool, dilute with 10 c.c. of dilute sulphuric acid (1—10), and then add gradually 40 c.c. of water. Heat to boiling, filter, and wash by decantation with dilute sulphuric acid (1—10), getting as little of the lead sulphate on the filter as possible. To the residue in the dish add 20 c.c. of strong ammonia, then make slightly acid with acetic acid. Boil until the lead sulphate is dissolved, then pour the liquid through the filter, having first moistened the paper with ammonia. Wash the filter with water containing ammonium acetate in solution, and finally once or twice with hot water. Cool the filtrate, and run in from a burette an excess of standard bichromate solution, stirring until the precipitate settles rapidly and the supernatant liquid has a yellow colour. Allow to settle for a few minutes, then filter, under pressure if possible; wash a few times, and titrate the filtrate against the standard ammonio-ferrous sulphate.

After a little practice the method can be carried out as above detailed in about thirty minutes. In case the ore is known to be free from bismuth and antimony, the method can be materially shortened. Instead of bringing the ore into solution with a mixture of nitric and sulphuric acids, nitric acid alone is used. After solution the acid is neutralised with an excess of ammonia, and then made acid with acetic acid: this dissolves any lead sulphate that has been formed. This solution is then immediately titrated with the bichromate and ammonio-ferrous sulphate solutions exactly as described above. The following table shows the agreement in the results obtained by this method:—

No.	Weight taken.	Calculated weight	Lead.
	Grm.	lead found. Grm.	
1	0.9983	0.8570	85.84
2	0.9987	0.8578	85.82
3	0.9997	0.8588	86.08
4	0.9806	0.8421	85.88
5	0.9996	0.8570	85.72
5	0.9971	0.8558	85.84
7	0.9975	0.8580	86.02
8	0.9936	0.8533	85.90

In general it may be said that the results are a trifle low. The mean of the amount of lead recovered in twenty determinations carried out by one of us was 99.6 per cent. of that taken.

We do not know that the modification as used by us has never before been tried, but our results appeared to possess sufficient value to warrant publication.—*Journ. Amer. Chem. Soc.*, xvii., p. 901.

Calculation of the Thermic Power of Coal according to Dulong's Rule.—G. Arth.—The author gives the analysis of seven varieties of coal, along with their calorific power as calculated and as determined by experiment. The greatest difference between the values is 1.85 per cent. of the value determined.—*Bull. de la Soc. Chim. de Paris*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Extra Meeting, January 23rd, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

PROFESSOR G. F. FITZGERALD, M.A., F.R.S., of Trinity College, Dublin, delivered the Helmholtz Memorial Lecture.

The position of the work of Helmholtz was considered with special reference to its chemical aspects, and the later work that had been grafted upon it. Some of the valuable points in the vortex atom hypothesis of matter were noticed, and some of its serious difficulties considered. Analogies on this hypothesis to the asymmetric carbon atom and to the benzene ring were pointed out. The applications of thermodynamics to chemistry were noticed, and a theoretically perfect semi-permeable diaphragm for non-volatile salts in solution, in which the actions at all points are known, was described. The theory that a substance in solution is like a substance in the gaseous state was criticised, and it was contended that from Helmholtz's work, and on dynamical grounds, the conditions could not be alike. The theory that there was combination between the solvent and body in solution was put forward as a complete explanation of the known phenomena of solution and electrolysis. It was pointed out how Helmholtz had, by his work, made important steps forward in several directions towards a dynamical explanation of Nature.

DISCUSSION.

The PRESIDENT said that there were two ways in which we may do honour to a great fellow worker who had passed away. The one is by a rehearsal of the great things he had done; the other—and perhaps this is rather that which the greatest would wish should happen after their own time has passed—is by a continuation of the lines of thought which they have started, and by following the work on which they have been engaged. Of the great variety of work which Helmholtz undertook—and there can scarcely be a greater scientific name than his, if the quality and variety of the work in which he engaged are taken into account—the lecturer this evening has naturally insisted on that side which Helmholtz himself selected as most appropriate when he was lecturing to this Society in the year 1881. These inquiries into the nature of molecules and other similar physical speculations which our lecturer this evening has touched upon, are of more recent growth. These are the problems which form our inheritance from that great man. Where work was so abundant there could scarcely be more than the enumeration of the great scientific results which we owe to Helmholtz. There are present this evening, besides many of our older members, several distinguished men of science who will say a few words on the subject of the lecture in proposing a vote of thanks to Professor Fitzgerald for the admirable exposition for which the Society is so much indebted to him.

Sir JOSEPH LISTER, P.R.S., said he had much pleasure in proposing a vote of thanks to Professor Fitzgerald for his profound and brilliant lecture. For his own part he felt himself in a world in which he was almost an entire stranger. These magnificent conceptions of physics must necessarily be nearly a *terra incognita* to the surgeon and physician. But physiologists and surgeons are deeply indebted to Helmholtz for what he did in their own domain. They recall with pride that Helmholtz was, in the first instance, a medical practitioner. It is an exceedingly remarkable fact in the case of such a profound and distinguished a physicist, that to the last he retained his love for his old subject, physiology. On this occasion it is not possible to allude to all that physiology owes to Helmholtz, but there are two questions to which reference might be made—his explanation of the accommodating

power of the eye for different distances, and what has been for physiologists and ophthalmic surgeons—although Professor Fitzgerald regarded it as a mere triviality in Helmholtz's achievements—the great invention of the ophthalmoscope, that beautiful instrument, by which the interior of the eye can be both illuminated and inspected. How much added to our knowledge of the physiology of the eye, and to the diagnosis of ophthalmic disease, and, consequently, to ophthalmic practice, and also to our knowledge of the various diseases which are found to be dependent upon or connected with affections of the eye—these discoveries, even if nothing else had been accomplished by Helmholtz, would be enough to secure the gratitude of physiologists and surgeons.

Dr. EDWARD FRANKLAND said he had great pleasure in seconding the vote of thanks. He expressed the feeling of every Fellow of this Society in saying that Professor Fitzgerald had given an hour's discourse of enormous interest and importance to chemists. It would take some time to study and analyse this discourse, and to adequately discuss it in detail; but, whilst chemists had listened to the discussion of numerous points of contact of the work of Helmholtz with their own department of science, they were led anew to admire the intellect of that great man who left, perhaps, no branch of human knowledge untouched during his career. Professor Fitzgerald's references to the application of vortex motions to the explanation of the chemical combination and valency were somewhat discouraging, and there were one or two other sections of his discourse which he hoped and believed were slightly too pessimistic. We may hope that when another four or five decades have passed we shall arrive at a point when these physical theories which appear to us at the present moment almost impossible of application to chemical science will then appear perfectly clear; and when in this room, possibly, another Helmholtz is to be honoured in this way, we shall have the satisfaction of seeing these beautiful physical theories applied with effect to those obscure chemical phenomena on which we are all so anxious to have more light thrown.

Lord RAYLEIGH said that he might be allowed to add his congratulations to the Society on having secured Professor Fitzgerald to give this most interesting lecture upon certain aspects of the work of Helmholtz. He has done it in a way that few others, indeed if any other, could do it. It is to be hoped that chemists will take into grave consideration the emphatic warning that Professor Fitzgerald has given, particularly as to the danger of supposing that there is any dynamical similarity between the condition of a gas and that of a dissolved substance in a liquid. He quite agreed with much that had fallen from Professor Fitzgerald upon that subject. There is possibly a risk of pushing formal analogies too far, and of supposing that there is a real dynamical similarity, whereas there is, perhaps, only a similarity in mathematical law. Many of the ideas that he has broached required prolonged thought and study to do justice to them. The new idea of the construction of a semi-permeable membrane composed of minute capillary apertures in a fluid of non-wettable material seems likely to throw great light upon a rather obscure subject. He had long been impressed with the idea that capillarity is very closely connected with many of the problems which we should like to understand better than we do, leading, perhaps, almost into the recesses of nature's chemical laboratory. His own familiarity with Helmholtz's work belonged to a different branch of the subject to that which Professor Fitzgerald had considered. Some thirty years ago he had studied with the ardour of youth Helmholtz's great work on the sensations of sound. Indeed, he had learned such German as he knew mainly from that book. It so happened that within the last year, in connection with work of his own, he had been revising and consolidating his knowledge of that work, and he was quite as much impressed as he ever was with the extraordinary force and ability with which all the difficult problems

that there arise are treated in turn by the distinguished author. Many of those who have written since upon the subject, and have criticised, perhaps too lightly, some of the positions assumed by Helmholtz—although, of course, no positions are to be considered as beyond criticism—seem to him not too be so familiar as they might be with the great work in which those positions were first of all set out. What Sir Joseph Lister and what Professor Frankland have said will be echoed by all who are acquainted with any side of Helmholtz's work, that everything that he touched was distinguished by his touch, and that there is scarcely any field of knowledge in which he has not, as it were, left his mark. All will agree that the object which the Society has had in view in commemorating the work of Helmholtz is a most excellent one, and that on this occasion it has been admirably attained.

Sir HENRY ROSCOE said that he could not say more than had been already said with regard to this lecture by Professor Fitzgerald, for which the Society was very grateful. He might add, perhaps, one personal reminiscence. He had the great honour and extreme pleasure, as President of the Society, of introducing Professor Helmholtz, in 1881, when he delivered the Faraday lecture here; and only a few months ago he happened to be at Heidelberg, and was speaking there to Professor Koenigsberger, the eminent mathematician, who was a very intimate scientific friend of Helmholtz. Koenigsberger spoke especially of Helmholtz's admiration, almost proceeding to reverence, for another great man who has passed away, who we are glad to reckon amongst the greatest of our countrymen, Clerk-Maxwell. Helmholtz used to talk of Clerk-Maxwell and his work as almost supernatural. Koenigsberger thought that Maxwell was in many respects superior as a scientific physicist to Helmholtz himself. This shows that Helmholtz, in his magnanimity and high character, was the last to belittle the work of others.

Professor ARMSTRONG said he would like to recall a fact to memory—that probably Helmholtz's Faraday lecture was the one Faraday lecture which was distinctly an original contribution, which we can be sure exercised a very important influence on the scientific world. A very large share of the attention which has been drawn to this subject of late years which van't Hoff, Arrhenius, and others have developed to such an extraordinary extent, has arisen out of that Faraday lecture by Helmholtz. Not only here but in Germany also it attracted very great attention, and was of very much consequence. To-night, again, the Society is to be congratulated very highly indeed that Professor Fitzgerald has most distinctly followed the example of the great man who gave the Faraday lecture in delivering a lecture of striking originality.

Professor POYNTING expressed his own gratitude and that of the other physicists present for the remarkable lecture to which they had had the privilege of listening.

The PRESIDENT said that there was one fact in respect to Helmholtz which had not been mentioned. Sir Henry Roscoe alluded to the fact of our own countryman, Clerk-Maxwell, having been ranked on the same plane as Helmholtz as a physicist. Helmholtz himself was half an Englishman. It is always said that in the making of great men the mother's share is a large one; and the mother of Helmholtz was an English woman. She was a Miss Penn, and was connected with the same family as the founder of Pennsylvania.

The vote of thanks on being put to the meeting was carried by acclamation.

Professor FITZGERALD, in replying to the vote of thanks, said that he regarded it as a very great honour to be asked to deliver this lecture, and felt very much flattered indeed by the way in which it had been received. He would feel fully compensated for any trouble it had cost him if it helped his fellow workers and honoured Helmholtz. To help others with information was not so high an aim as to help them with moral ideals. The former was his aim; the latter was provided for him by the sympathy

and encouragement of the Chemical Society. He thanked them for it.

PHYSICAL SOCIETY.

Annual General Meeting, February 14th, 1896.

Captain W. DE W. ABNEY, President, in the Chair.

THE CHAIRMAN, after referring to the position of the Society, called upon the Treasurer to read the balance sheet.

After a discussion on the financial status of the Society, in which a number of members took part, the ballot was held for the election of a President and Council for the ensuing year. The following gentlemen were declared duly elected:—

President—Capt. W. de W. Abney, R.E., C.B., D.C.L., F.R.S.

Vice-Presidents—Shelford Bidwell, M.A., LL.B., F.R.S.; Maj.-Gen. E. R. Festing, R.E., F.R.S.; Prof. J. Peiry, D.Sc., F.R.S.; G. Johnstone Stoney, M.A., F.R.S.

Secretaries—T. H. Blakesley, M.A., M.Inst.C.E., 3, Eliot Hill, Lewisham, S.E.; and H. M. Elder, M.A., 50, City Road, E.C.

Treasurer—Dr. E. Atkinson, Portesbury Hill, Camberley, Surrey.

Demonstrator—C. Vernon Boys, F.R.S.

Other Members of Council—Walter Baily, M.A.; C. V. Burton, D.Sc.; L. Fletcher, M.A., F.R.S.; R. T. Glazebrook, M.A., F.R.S.; Prof. A. Gray, M.A.; G. Griffith, M.A.; Prof. G. M. Minchin, M.A., F.R.S.; Prof. W. Ramsay, Ph.D., F.R.S.; Prof. S. P. Thompson, D.Sc., F.R.S.; and Prof. S. Young, D.Sc., F.R.S.

THE CHAIRMAN read an obituary notice of the late Rt. Hon. T. H. Huxley.

A vote of thanks to the auditors was proposed by Prof. Carey Foster, seconded by Mr. Enright, and carried unanimously.

A vote of thanks to the officers was proposed by Prof. A. Gray, seconded by Mr. Rhodes, and carried unanimously.

A vote of thanks to the Chemical Society for the use of their rooms was proposed by the Chairman, and carried by acclamation.

The meeting was then resolved into an Ordinary Science Meeting, and

A paper "*On the Determination of High Temperatures by the Meldometer*," by Prof. RAMSAY and Mr. EUMORFOPOULOS, was read by the latter.

The meldometer, an instrument invented by Dr. Joly, of Dublin, consists essentially of a thin platinum strip, which can be heated by the passage of an electric current. Small fragments of a solid substance are placed on the platinum strip, and the temperature at which they melt is deduced from the length of the platinum strip, which has been previously calibrated by means of solids of known melting-point. The authors have used gold for the purpose of calibrating the strip, and have assumed Violle's value, 1045° C., for the melting-point of gold. A number of measurements have been made of the melting-points of the salts of sodium, lithium, strontium, barium, calcium, and lead. The results obtained, however, differ considerably from those of Heycock and Neville, and the authors have not been able to account for these differences.

Prof. RAMSAY said the chief advantage of the meldometer was that only a very minute fragment of the substance was required for the measurement, so that extreme purity of the sample could be secured. There was the disadvantage, however, that many substances undergo some change when heated in air. In reply to a question from Mr. Blakesley, Prof. Ramsay said that the property

of the platinum which was used to measure the temperature was its expansion.

Mr. CAMPBELL asked whether the zero of the instrument was found to be constant. In Cardew voltmeters it often took several hours for the needle to come back to zero after heating.

Mr. EUMORFOPOULOS, in reply, said that the zero was constant to within a quarter of a degree.

Prof. RAMSAY also exhibited a small direct-vision spectroscope, in which the eye-piece is moved in a plane perpendicular to the axis of the instrument by means of a micrometer screw. This form of spectroscope is found to be of great utility in verifying the position of lines in the spectrum.

NOTICES OF BOOKS.

Elementary Agricultural Chemistry and Zoology. By Sir CHARLES A. CAMERON, Professor of Chemistry and Hygiene, Royal College of Surgeons. Dublin: Hodges, Figgis, and Co. (Ltd.). London: Simpkin, Marshall, and Co. (Ltd.). 1896.

WE have here a very compact and clearly-written work on chemistry and geology as they especially concern the farmer and the horticulturist,—in a word, the manufacturer of food. One of its great merits is that it explains the technical terms so freely—perhaps too freely—used by botanists and vegetable physiologists.

The author first gives an account of the chemical elements, atoms and their combinations, equivalents, molecules, atomicity, symbols, double decomposition, chemical formulæ, and nomenclature. He then proceeds to give a similar survey of the development of plants, the parts of the plant, protoplasm, the chemical composition of plants, their atmospheric food, and the nitrifying action of bacteria. The food of plants on the soil forms the subject of Chapter VIII.

The formation of soils is ably explained. The constituents of soils and their varieties are next described. The composition of a common soil is given as:—

Organic and volatile matters ..	8.60
Alumina	7.00
Ferric oxide	4.40
Lime	1.00
Magnesia	0.80
Potash	0.40
Phosphoric acid	0.22
Sulphuric acid	0.15
Chlorine	0.10
Silica and insoluble silicates ..	77.93

Concerning sandy soils we find a very suggestive hint:—"The soils on which the finest clarets in France are produced are incapable of yielding a wheat crop." It is admitted that worms, and even microscopic organisms, are powerful factors in producing fertility of soils."

Next follows the geological classification of the rocks, with remarks on the agricultural value of the soils, furnished by their comminution and decomposition. We are reminded of the facts that the millstone grit produces barren soils, and that those of the sandstones of the coal-measures are worthless,—for instance, the lands to the east and north east of Manchester. On the contrary, the Triassic rocks (keuper marls) form splendid meadows and orchards. The Lias formation yields fine pastures, on which the Stilton and other superior cheeses are produced. The chalk districts do not rank high from an agricultural point of view.

We find mention of the degradation of our climate since the tertiary period, and of the glacial epoch (or epochs?) which succeeded.

Chapters XIX., XX., and XXI. give a view of the

geology of England, Ireland, and Scotland. In discussing the improvements of soils the author gives a caution concerning liming, subsoiling, and irrigation, but recommends afforesting, which in Britain is almost rendered impossible by the law. If a useless region is planted it is at once heavily smitten by local taxation, a quarter of a century before the returns come in.

Sir C. Cameron has found that coprolites finely ground produced a better crop of turnips than an equal money's worth of superphosphates.

This book is not only useful in itself, but will enable an attentive reader to study larger works with advantage.

Chemistry for Engineers and Manufacturers. A Practical Text-Book. By BERTRAM BLOUNT, F.I.C., F.C.S., Consulting Chemist to the Crown Agents for the Colonies, and A. G. BLOXAM, F.I.C., F.C.S., Head of the Chemistry Department, Goldsmith's Institute, New Cross. Volume I.—Chemistry of Engineering, Building, and Metallurgy. Large 8vo., pp. 244. London: Charles Griffin and Co. (Ltd.), Exeter Street, Strand. 1896.

THIS work consists of two volumes, each of which it is announced will be sold separately. This is a judicious arrangement, since each of them appeals in a considerable degree to a distinct class of readers. Vol. I., now before us, is addressed to mechanical engineers, architects and builders, and to all engaged in the erection of plant and the production of power.

The first chapter treats of the chemistry of the chief materials of construction, classified as stones, bricks, cements, &c, structural metals, and roofing materials. Next follow useful instruction on the strength, permanence, and preservation of materials.

The chemistry of the sources of energy is considered in the second chapter. The author seems to forget that in hot and cloudless regions,—e.g., Australia,—the kinetic energy pouring from the sun can be utilised industrially without the drawback of coal-smoke and coal-miners. In the account of gaseous fuels we do not see that reference is made to the deleterious character of CO, which forms so important a constituent of coal-gas, and to its removal by the Crookes process. The applications of the electric furnace in metallurgy are scarcely appreciated as they merit. The direct transformation of heat into electric energy without the tedious and wasteful interposition of the steam-engine is not overlooked.

The chemistry of steam-raising forms the subject of Chapter III., and involves a careful consideration of hard waters, their behaviour in boilers, and the means for removing the objectionable saline matter,—in other words, for softening and purifying boiler-water. Anti-incrustating mixtures, it is recommended, should be sold under their own names and at their own market-prices.

Lubricants are discussed in Chapter IV. The very correct conclusion is drawn that every different kind of bearing needs a different lubricant to enable it to run with the least friction. Contrary to a common prejudice, olive-oil is not the best lubricant, as it readily becomes rancid,—i.e., acid. Mineral oils, used as lubricants, should have a flashing-point not below 150°, and in cylinder lubrication not below 200° to 250°. Fatty oils, it must be remembered, if diffused over fibrous and pulverulent substances, have the dangerous property of occasioning what is called "spontaneous combustion." One of the most dangerous substances, if thus moistened with a fatty oil, is weighted or loaded silk—a property of which fire-insurance companies should beware.

The second part of the volume treats of metallurgy. Metalliferous ores are classified into—

1. Such as occur native, pure, and alloyed, copper, bismuth, mercury, silver, gold, platinum and its group, though it must be remembered that copper and mercury are commonly found as true ores, i.e., in combination with non-metallic elements.

2. Oxides; iron, copper, tin, zinc, manganese, and aluminium.
3. Sulphides; lead, copper, zinc, antimony, and mercury. Iron occurs in vast quantities in combination with sulphur, but such ores as pyrites are generally used as sources not of iron, but of sulphur.
4. Carbonates; copper, zinc, lead, and iron.
5. Haloids, silver; aluminium and sodium.
6. Arsenides and antimonides; nickel and cobalt.

It is remarked that nickel is also found in quantity as a double silicate.

Platinum has latterly been found as an arsenide, PtAs₂, at Sudbury, in Canada. The mineral is known as sperrylite.

To notice critically the processes indicated for winning each metal would far exceed the space at our disposal. We may say that the first part of this volume will be a valuable guide to persons engaged in designing chemical works and plant, whilst the second part is a key to more special metallurgical studies.

CORRESPONDENCE.

THE X RAYS.

To the Editor of the Chemical News.

SIR,—I notice in CHEMICAL NEWS, vol. lxxiii., p. 73, it is stated that a correspondent, whose name is not mentioned, has suggested the use of a vacuum tube consisting, not of glass, but of aluminium, for the production of Prof. Röntgen's X rays. I take the liberty of drawing your attention to the closing words of Mr. Swinton's article in *Nature*, Jan. 23, which show that Mr. Swinton had thought of using aluminium.

"Further, having regard to the great opacity of glass, it seems probable that where ordinary Crookes tubes are employed a large proportion of the active radiations must be absorbed by the glass of the tube itself. If this is so, by the employment of a tube partly constructed of aluminium, as used by Lenard, the necessary length of exposure could be reduced."—I am, &c.,

CLAYTON BEADLE.

February 16, 1895.

ESTIMATION OF INSOLUBLE PHOSPHATE.

To the Editor of the Chemical News.

SIR,—Mr. Edwards admits, in his letter to you on the above subject (CHEMICAL NEWS, vol. lxxiii., p. 72), that where there is any quantity of iron and alumina present in the material the volumetric uranium method of estimation of the insoluble phosphates, as proposed by himself, does not give reliable results. He goes on to say, however, that in ordinary cases the amount of oxide of iron and alumina is usually very small. With this statement I cannot agree; it is only in comparatively few cases that iron and alumina are not present in relatively large quantities in the "insoluble phosphate," as compared with the amount of phosphoric acid. The materials of which the average superphosphate are manufactured will rarely contain less than 2 per cent of oxide of iron and alumina. This, roughly speaking, would equal about 1 per cent on the manufactured article. Practically all of this would be found in the "insoluble." 1 per cent of oxide of iron and alumina would equal (taking half as iron and half as alumina), on calculation to normal phosphates, 2.15 per cent; or, in other words, about 50 per cent of the total insoluble phosphate usually present in superphosphates.

This is a factor, I take it, which we cannot afford to ignore when dealing with this uranium process.

I fully appreciate the advantages of a quick estimation of the "insoluble phosphate" in works, where the results

are so often required in a hurry as a guide to future operations, but would prefer to rely upon calculation to attain this result, rather than a process which I am afraid would be extremely liable to give very uncertain results.—I am &c.,

GEO. H. ALLIBON.

Messrs. Richardson Bros. and Co.'s
Manure Works, Belfast, February 18, 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 4, January 27, 1896.

Utility in Human Pathology of Photographs taken by the X Rays.—MM. Lannelongue, Barthélemy, and Oudin.—Already inserted.

Nomination.—Prof. Rouché was elected a "free member" of the Academy, *vice* the late Baron Larrey.

Some Properties of the Rays of Röntgen.—Jean Perrin.—Already inserted.

Dark Light.—Gustave le Bon.—Already inserted.

Action of Heat on Mercurous Iodide.—Maurice François.—From the manner in which mercurous iodide behaves under the action of heat, the following results follow:—We cannot melt mercurous iodide without decomposing it. Mercury separates out at the bottom of the vessel. The supernatant mass is a mixture of mercurous and mercuric iodides. We can, without causing a decomposition, *i.e.*, without a separation of mercury, melt mixtures rich in mercuric iodide, such as the mixture of 2 mols. mercuric iodide and 1 mol. of mercurous iodide. Neither the melting-point nor the ebullition-point of mercurous iodide can be exact. We cannot, by simple fusion, obtain crystals of mercurous iodide free from mercuric iodide. Yet, as mercuric iodide has a lower solidification-point than mercurous iodide, the melted mixture of these two substances gives in the first place, whilst cooling, crystals of mercurous iodide. By removing the portion which remained liquid, I have found that we may obtain by fusion crystals of mercurous iodide containing interposed variable quantities of mercuric iodide.

Absorption of Light by Solutions of the Indophenols.—M. Bayrac and Ch. Canichel.—One of us has prepared a series of indophenols derived from ten different phenols. They are soluble in ether, alcohol, benzene, acetic acid, acetic ether, and ligroine. The colour of the solution differs with the solvent; the same solvent gives with the different indophenols solutions of the same colour. If we intercalate these solutions in the path of luminous rays which illuminate the slit of a spectroscop, we remark that they all give a spectrum formed of a red band very brilliant and narrow, and of a much broader band of low intensity composed of green, violet, and indigo. The region of the spectrum between these bands is absorbed, except for very shallow strata or exceptionally low concentrations. The authors have arrived at the following result:—If we dissolve weights of each substance proportional to the molecular weights in an equal volume of the same solvent, the red band occupies the same position in the different spectra obtained.

Compounds of anhydrous Aluminium Chloride with the Phenols and their Derivatives.—G. Perrier.—Not suitable for useful abstraction.

Russian Aniseed Oil.—G. Bouchardat and M. Tardy.—Russian aniseed oil consists chiefly of anethol. There are also present anisic camphor, called by Wallach *fenchene*, and anisic acetone, and a small proportion of anisic acid.

Production of Pure Gaseous Formic Aldehyd.—A. Brochet.—The author uses as his material trioxymethylene, which is dissociated by heat, yielding formic aldehyd free from carbon monoxide.

Bulletin de la Société Chimique de Paris.

Series 3, Vols. xiii.-xiv., No. 16 and 17, 1895.

Reduction of Nitric Oxide by Moist Iron or Zinc.—Paul Sabatier and J. B. Senderens.—From the experiments of the authors it appears that the nitric oxide is reduced, not merely to nitrous oxide, but to a considerable extent to free nitrogen.

Reduction of Nitrous Oxide by Metals in presence of Water.—Paul Sabatier and J. B. Senderens.—Nitrous oxide in solution is reduced to the state of nitrogen by magnesium, zinc, iron, and even cadmium, with the simultaneous formation of a little aminonia.

Volatilisation of Carbon.—Henri Moissan.

Reduction of Alumina by Charcoal.—Henri Moissan.

Study of the different Varieties of Graphite.—Henri Moissan.

Displacement of Carbon by Boron and Silicon in Melting Cast-iron.—Henri Moissan.

Study of the Graphites of Iron.—Henri Moissan.

Preparation of Sprouting Graphites in the Electric Furnace.—Henri Moissan.—The last six papers have been duly noticed under the *Comptes Rendus*.

Variations of the Rotatory Power in the β -Methyladipic Series.—P. Freundler.—This paper does not admit of useful abstraction.

Campholenic Derivatives. Campholenonitriles and Campholenamides.—A. Béhal.—This paper and that succeeding, by the same author, "On the Campholenic Acids and Campholenes," are not suitable for abstraction, and are scarcely of sufficient importance for insertion in full.

Non-existence of Stereoisomerism in the Amino-butenediorcic Derivatives.—R. Thomas-Mamert.—The derivatives in question do not exhibit stereoisomerism.

Ethyl-aminobutenamidoates.—R. Thomas-Mamert.—Not suitable for abstraction.

New Preparation of Glycerose.—M. Fonzes-Diacon.—The author has obtained this aldehyd by dehydrogenating anhydrous glycerin with mercuric chloride.

Revue Universelle des Mines et de la Metallurgie.

Series 3, Vol. xxxii., No. 1.

On a New Procedure for the Extraction of Gold from Tailings, Slimes, and Concentrations.—B. de Wilde.—The author describes a modification of the cyanide process employed in the Transvaal, the United States, and New Zealand. His procedure consists of three operations—the solution of the gold, the recovery of the excess of cyanide, and the precipitation of the gold. He does not find that the addition of oxidising bodies to the solution of cyanide fails to produce any serious benefit. The mean consumption of cyanide is said to be 2 lbs. per ton of tailings; this quantity is capable of much reduction, probably down to $\frac{1}{2}$ lb. The excess of cyanide is recovered by adding to the liquid ferrous sulphate, until a few drops of the filtrate begin to give a blue colour on the addition of some drops of a solution of potassium ferricyanide. The gold remains in solution in the state of potassium auro-cyanide. The precipitation of the gold is based upon the following principle:—In a solution containing the double potassium auro-cyanide, we precipitate all the cyanogen as aurous cyanide, and cuprous cyanide on acidifying the solution by means of sulphurous acid, and then adding a solution of copper sulphate. The least excess of this salt effects the absolutely complete precipitation of the gold.

MISCELLANEOUS.

A Battle for a Word.—A controversy is at present raging in the pages of the *Chemiker Zeitung*. A certain firm lays claim to the exclusive right of applying the name "phenacetin" to one of its products,—a demand the more remarkable as the method of preparing this drug is not patented in Germany.

The Humus Theory in Agriculture.—In the *Chem. Zeitung* Dr. Gigli reviews a work by Prof. Adolfo Casali, on the part played by humus in the fertilisation of soils. The author shows that Saussure's humus theory contains a phase of truth which cannot be neglected, and that humus in fact contributes largely to the nutriment of plants, as it forms an excellent medium for microbial life.

Further Details on Argon and Helium.—Lord Rayleigh and Professor Ramsay have examined the gases given off from the hot springs of Bath, and find that they contain less argon than atmospheric air, but also helium. The gases from the Buxton springs contain about 2 per cent of argon, but the presence of helium is questionable. According to the latest results of the discoverer, argon is not a mixture, and cannot be an allotropic variety of nitrogen.

The X Rays.—A report is in circulation, though we cannot say on whose authority, that a Professor of the University of Perugia has rendered Prof. Röntgen's rays visible by means of a newly-invented instrument, which its author, Prof. Salvioni, names the iristoscope. G. d'Imperilla announces, in the *New York Electrical Engineer*, a process for secretly seeing and photographing objects at night or in darkness. A judicious reserve will be useful in speaking of any application of the X rays.

The Philadelphia Museums.—There are now established at Philadelphia a group of Museums, economic, educational, commercial, and scientific in their character and objects. Their purposes—those especially of the "Commercial Museum"—seem to be very similar in character to those of the Imperial Institute of London, as originally planned. It does not appear that any of them are intended to be perverted into places of amusement.

MEETINGS FOR THE WEEK.

- MONDAY, 24th.—Society of Arts, 8. (Cantor Lectures). "Chemistry of certain Metals and their Compounds used in Building, and the Changes produced in them by Air, Moisture, and Noxious Gases, &c.," by Prof. J. M. Thomson, F.R.S.E.
Medical, 8.30.
- TUESDAY, 25th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.
Society of Arts, 8. "The Palette of the Potter," by William Burton, F.C.S.
Medical and Chirurgical, 8.30.
Institute of Civil Engineers, 8.
Photographic, 8.
- WEDNESDAY, 26th.—Society of Arts, 8. "The Standard of Musical Pitch," by A. J. Hipkins.
British Astronomical, 5.
Geological, 8.
- THURSDAY, 27th.—Royal, 4.30.
Royal Institution, 3. "Some Aspects of Modern Botany," by Prof. H. Marshall Ward, F.R.S.
Society of Arts, 4.30. "The Tobacco Industry of India and the Far East," by C. Tripp.
Institute of Electrical Engineers, 8.
- FRIDAY, 28th.—Royal Institution, 9. "On Marine Organisms and their Conditions of Environment," by Dr. John Murray.
Physical, 5. Experiments with Incandescent Lamps, by Sir David Salomons. "On the Alternating Current Arc," by Messrs. Fleming and Petavel.
- SATURDAY, 29th.—Royal Institution, 3. "Light," by Lord Rayleigh, F.R.S., &c.

TO CORRESPONDENTS.

H. A. le Hill.—Communication received. Please forward address.

NOTES AND QUERIES.

** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Quantitative Separation.—What is the best book to get on the quantitative separation of organic acids, alcohols, and ethers, such as are in fermented liquids of varying ages?—A. B.

Carbonic Acid.—Can any reader please answer me the following questions about carbonic acid? Assuming that when the gas is in the liquid state and in the presence of water or moisture it is capable of combining chemically to form the hydrate, in this state can it pass from the liquid to the gaseous without breaking up the combination? If so, would there be any action when the (hydrated) gas is passed over fused CaCl_2 or through conc. H_2SO_4 when under varying pressures?—F.C.S.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1892.

ON THE APPLICATION OF RÖNTGEN'S RAYS IN SURGICAL DIAGNOSIS.

By MM. LANNELONGUE and OUDIN.

It is necessary to ascertain to what degree the new rays can traverse the most compact parts of the human body, to show the state of the hard portions found there. To this end we have taken the thigh and the knee,—the first time, we believe, that the attempt has been made. The two subjects had tedious affections of this region of the body, and it was interesting to know if the diagnoses which had been carefully made beforehand would be confirmed by the new method of investigation.

The first subject is now cured of an osteo-arthritis of the left knee, of a tuberculous nature, which had required three years of successive treatment.

The second photograph which we present is that of the thigh of a child of 8 years of age, who had suffered from osteitis of the femoral diaphysis. He is now cured, and walks perfectly well.

The examination with the new light did not afford any novel information which had escaped notice, but it confirmed in all points the indications arrived at clinically.—*Comptes Rendus*, cxxii., p. 283.

INFLUENCE OF THE CHEMICAL NATURE OF SUBSTANCES, AND THEIR PERMEABILITY BY THE RÖNTGEN RAYS.

By MAURICE MESLANS.

NUMEROUS experiments have demonstrated that certain bodies are transparent to the radiations emitted by the Crookes tube, whilst others present as regards these rays a relative opacity. I have undertaken to examine what is the relation which may exist between the transparency of these substances and their chemical nature, and if the Röntgen rays may not furnish a new means of investigation in the domain of chemistry. I will here merely indicate the most striking of the results which I have obtained: they are manifest on an examination of the photographic proofs which I submit to the Academy, and which refer to about fifty substances, simple and compound. These results, though incomplete, seem to me to offer some very definite conclusions, and determine me to pursue this study further.

The transparency or opacity of bodies to the X rays is not absolute; the influence of thickness has been already demonstrated, and the rôle of density has been examined. The specific chemical nature appears to me to present a very considerable influence. I have compared together the various non-metallic bodies as well as their acid derivatives, and the salts, metallic or organic, which they yield. My experiments have related chiefly to organic bodies, and to their essential element, carbon.

I have been hitherto able to establish the extreme transparency not merely of carbon in its different states, compared to those of other non-metals, the slight opacity of organic compounds when along with carbon they contain merely the gaseous elements, hydrogen, oxygen, and nitrogen. Still this transparency is far from being uniform, and presents very various degrees which appear connected with the chemical function of these bodies.

The photographic proofs which accompany this me-

moir have been obtained by shutting up a photographic plate in a frame for negatives, and arranging upon the little board which covers the plate the substances whose transparence it was desired to study, lighting up the whole with a Crookes tube, placed at a distance of 20 c.m. After an exposure of thirty minutes, the plate and development gave silhouettes of the bodies experimented upon, the relative intensities of which measured their transparence.

Diamond, graphite, anthracite, sugar-charcoal, give a faint tinge of a tonality similar to that of wood or of paraffin of an equal thickness, whilst sulphur, selenium, phosphorus, iodine, afford very strong images of great opacity.

The organic substances, ethers, acids, nitrogenous substances, were easily traversed by the X rays, and gave images scarcely perceptible; but the introduction into the organic molecule of a mineral element, such as iodine, chlorine, fluorine, sulphur, phosphorus, &c., gives to the molecule a great opacity.

The sulphates of the alkaloids are in this case. In like manner iodoform is very opaque, whilst the alkaloids, picric acid, magenta, and urea are very opaque. Phthalyl fluoride is much more opaque than phthalic acid, although the molecular weights of the two bodies approximate very closely. The metallic salts possess a great opacity, but which varies with the metal and the acid.

These results are corroborated by the photography of hands and of small entire animals executed by Professor Röntgen and others. In these proofs the muscles remain transparent. They are, in fact, substances formed entirely of carbon, hydrogen, oxygen, and nitrogen. The bones, on the contrary, give strong images. The opacity is due to the mineral elements which they contain.

The differences in the chemical constitution of the matters forming nerves, blood, &c., will doubtless permit us to obtain their photographic images, thanks to their unequal transparency.

I hope to carry out with more exactitude these researches on definite chemical species, and I purpose studying the relation between the chemical constitution of bodies and their degree of transparency to the Röntgen rays. At present the result which seems established is the transparency of carbon and its compounds with hydrogen, oxygen, and nitrogen, and the great opacity occasioned by the introduction into the organic molecule of other mineral elements, especially Cl, S, P, and above all I.—*Comptes Rendus*, cxxii., p. 309.

APPLICATION OF RÖNTGEN'S METHOD.

By ALBERT LONDE.

I HAVE the honour of submitting to the Academy a photograph obtained by Röntgen's method. This proof represents the pinion of a pheasant killed by shooting. The fracture of the bone is perfectly visible; we distinguish a detached fragment of bone, and a shot which has been embedded in the flesh.

I wish to point out the perfect transparency for the X rays of the photographic image as it is generally obtained. The heavy shades which in the ordinary processes do not allow the light to traverse, save in a rudimentary manner, appear as transparent to the X rays as to the large light parts. To verify this fact we have operated on films of celluloid, which does not arrest the X rays like glass.

On the other hand, we have exposed plates of different sensibilities, during equal times and at equal distances. We have decided that the impression was much more energetic on the rapid plates, and that the strength of the image was directly in proportion to the sensitiveness of the preparation.

The photographic plates therefore behave with the X rays exactly as with light.—*Comptes Rendus*, cxxii., p. 311.

ON A
MECHANICAL ACTION EMANATING FROM
THE CROOKES TUBE ANALOGOUS
TO THE PHOTOGRAPHIC ACTION DISCOVERED
BY RÖNTGEN.

By MM. GOSSART and CHEVALIER.

WE have the honour of pointing out to the Academy a field of mechanical force manifested in the interior of the Crookes radiometer when fixed opposite to a Crookes tube.

We wished, in a course of public lectures on the radiations of electric lamps, to introduce Röntgen's X rays, the cathodic rays of Crookes, and the stratified light of Abria, which led Crookes to his discovery by the augmentation of the strata. It seemed to us logical to manifest at a distance the heating of the Crookes tubes by means of his radiometer. Our surprise was great on seeing the vanes of the radiometer not merely remain motionless before a very hot tube, but, even if once set in motion by means of extraneous heat, stop in front of the tube with a very fixed orientation, and after pendulum oscillations which are the more rapid as their distance from the tube decreases.

It is clear that we were confronted with a mechanical action due to a field of force erected in the radiometer, and antagonistic to that of heat.

We fell to work to verify the existence of this field of force around the Crookes tube, by studying it with the radiometer as to direction and intensity, and proving, upon some twenty substances, that this force traverses the same media, or is arrested by the same substances, as the X rays.

Furthermore, when once the radiometer is placed in the Crookes field, and only then, we found that the field, viscous in some degree, which stops the vanes, is modified by currents, especially by that of the exciting coil of the Crookes tube, modified by substances, electrified statically, and is lastly disturbed energetically by a magnet. On moving a magnet around the sides of the radiometer, we as it were unscrew the vanes, and render them anew obedient to the source of heat.

Thus we may cause, simultaneously or successively, the X rays, heat, and electrostatic, electro-dynamic, and magnetic forces, to enter into action upon the vanes of the radiometer.

It seems to us, therefore, that we have a convenient instrument with qualitative and quantitative indications for making new investigations on the radiations, still mysterious, which emanate from the Crookes tube,—an emission following the exciting sources, the transmission, &c.

We therefore set up on a Melloni stand:—1. A Locatelli lamp. 2. The radiometer at 30 c.m. from the lamp, so as to give about fifteen rotations per minute. 3. The Crookes tube, movable on its right axis by means of an index which shows, on a graduated circle, the various directions of the axis of the cathodic sheaf of rays.

As soon as we project the cathodic rays there is an arrest of the vanes, and not in consequence of a dissymmetry of the system, since we have seen sometimes the one and sometimes the others take the axial direction of equilibrium. Unfortunately we have not yet been able to procure an apparatus with the vanes.

If we extinguish the Crookes tube, the stoppage persists for about five minutes in spite of the constant action of the Locatelli lamp. A fantastical and perhaps suggestive means of setting them again in motion is to project anodic rays, bringing the tube of the radiometer within a few millimetres. The vanes undergo at first an impulse in the direction opposite to the normal movement, which they afterwards resume.

We have determined a first line of the level of the field by actuating our single Crookes tube with a large Ruhmkorff's

coil and a primary current of 20 volts. This line is determined by the cessation of the stoppage; it is normal to the direction of one of the pairs of vanes; its maximum distance from the tube was 3 c.m. in front of the axis (distance from side to side), and it coincided with the tube towards the centre of the concave cathode.

On enclosing the tube with a circular photographic film, shut up in a paper case lined with metal letters, we were able to verify approximatively the concordance of the two fields.

Relatively to the sources, we can only make definitely this remark: the inertia of five minutes in the stoppage, which is manifested with a Ruhmkorff coil, is not obtained with a Wimshurst machine.

Our experiments were particularly directed to the transparency of the substances for the force of the photographic action. The following substances were very pervious for both radiations:—Pasteboard, ebonite, felt (layer of 2 c.m.), sulphur, paraffin (1 c.m.), wadding, &c. With equal thickness the action is propagated further through paraffin than through air.

As opaque bodies we indicate, in the order of decreasing opacity,—Lead, copper, aluminium, ivory, retort-coke.

This note may be the point of departure of a series of researches which we hope to pursue to study the field of the Crookes tube with the radiometer.—*Comptes Rendus*, cxxii., p. 316.

INCREASE OF THE PHOTOGRAPHIC YIELD
OF THE RÖNTGEN RAYS BY MEANS
OF PHOSPHORESCENT ZINC SULPHIDE.

By CHARLES HENRY.

If we apply on the surface of a photographic plate opposite to the gelatino-bromide a layer of my phosphorescent zinc sulphide, of from 0.5 to 1 m.m. in thickness, having care to reserve half the plate taken longitudinally, and if we expose in a frame provided with a curtain successive bands of this plate to the light of a candle for increasing times, we naturally obtain, after developing and fixing, a series of tints of decreasing intensities, but we find between the two halves of the plate (that which has received zinc sulphide on the glass, and that which has not received it) a notable difference in the intensity of the grey tones; we see, e.g., on one of the proofs thus obtained, that the blackest half-band of those behind which there is no zinc sulphide has the same intensity as a half-band coated beneath with zinc sulphide, but exposed for only one-seventh of the time.

The ultra-violet rays pass, therefore, through the gelatino-bromide and the glass, and act upon the zinc sulphide, and the sulphide continues the reductive action by its own radiations, even on plates not sensitised to a yellowish green, then by its most refrangible radiations and by others, as will be seen at the end of this paper.

The Röntgen rays often behave quite differently in these conditions; if we expose to this radiation with the ordinary arrangement a gelatino-bromide plate sulphuretted in certain regions on the side opposite to the sensitive surface, we find on some plates no difference between the intensities of the parts the opposite side of which has been sulphuretted, and the intensities of those when the opposite side has been left untouched.

As the zinc sulphide is very easily saturated with the light of the Röntgen radiation, and as in certain cases this sulphide is acted on through the glass and the gelatino-bromide, we must conclude that, in the plates in question it is not the gelatino-bromide but the glass which plays the part of absorbent. This is a new demonstration of the difference between the Röntgen rays and the ultra-violet rays, and the importance which must be ascribed to the glass and to its thickness in the cases where we

wish to sensitise the plates to these rays by the application of zinc sulphide to the opposite side of the plate.

If we photograph by the ordinary procedures, by daylight, an image painted with phosphorescent zinc sulphide, the parts to which the greatest thicknesses of the sulphide have been applied appear on the negative in white, more or less intense. On examining the behaviour of an object covered with phosphorescent zinc sulphide as regards the Röntgen rays, I have observed the remarkable fact of a striking increase of the photographic efficacy of the rays.

In a first experiment I photographed two fingers, the fore and the middle finger, the fore-finger having been coated with sulphuretted vaseline. It was found that all that portion of the plate which surrounds the shadow is blacker than the rest.

In a second experiment I placed on the photographic plate, wrapped in needle paper, an iron wire, and on this iron wire, in succession from the left to the right, a piece of 0.05 frc. intact, a piece of 0.10 frc. coated with sulphide on its anterior surface, a piece of 0.010 frc. coated with sulphide on its anterior surface, a piece of 0.05 frc. coated with sulphide on its posterior surface, a 5-frc. piece in silver coated with sulphide on the larger part of its anterior surface; lastly, a small optical trough, cylindrical, divided into two compartments, and containing in the right-hand compartment a solution of quinine sulphate. The plate being developed and fixed after an exposure of forty-five minutes gives a very distinct shade of the iron wire behind the coin of 0.10 frc. coated with sulphide on its anterior surface, a shade rather less definite behind the portion of the coin of 0.05 frc. coated with sulphide on its posterior surface (the shadow of this piece coming up lighter than the others), a shadow less distinct also behind the portion of the 5-frc. piece coated with sulphide (silver being under equal conditions more transparent than bronze); on the other hand, there appeared no shadow of the wire behind the sou left intact, and behind the portion of the 5-frc. piece not coated with sulphide. Quinine sulphate did not exert any appreciable effect.

This experiment proves that it is possible, by coating with phosphorescent zinc sulphide bodies capable of absorbing Röntgen's rays, to render visible on the photographic plate objects situate behind such bodies and otherwise invisible. The zinc sulphide fulfils the office of a supplementary actinic source; it converts into photographic rays Röntgen's rays which are inert in this respect, a new proof of the complexity of the radiations emitted by the Crookes phial.

It is probable that other sulphides besides the phosphorescent zinc sulphide possess this property. I have not had the leisure to try them; but the great inalterability of the phosphorescent zinc sulphide secures for it an incontestable superiority over all other artificial phosphori.

I have likewise had occasion to verify, in the phosphorescent zinc sulphide, a hypothesis of Henri Poincaré. "May we not then ask ourselves if all bodies whose phosphorescence is sufficiently intense do not emit in addition to luminous rays the X rays of Röntgen, whatever may be the cause of their fluorescence?"

I have exposed for a second to the light of a magnesium ribbon a parallelepipedal ingot of aluminium, 0.145 metre long, 0.145 metre broad, and 0.006 metre thick, resting on a small support of blackened cardboard. On the outside for a length of 0.06 metre, I coated it with zinc sulphide; then I left intact, externally and internally, a surface of 0.05 in length; lastly, I coated the ingot with this same sulphide internally on a surface of 0.038 in length, almost entirely shaded from the light of the magnesium, except at the edges. I placed between the ingot and the photographic plate, covered with a double sheet of needle paper, the above-mentioned iron wire. After developing and fixing the negative presented a slight white silhouette of the wire on the rectangular black ground of the shadow of the ingot. The difference of

tints imperceptible in the non-sulphuretted portion of the aluminium plate is more appreciable in the portion of the plate corresponding to the portion of the plate sulphurised below. In the same manner, after exposing the ingot to diffused daylight from three to five hours on a plate covered with a double sheet of needle paper, I obtained a very distinct veil of the plates visible, as far as the confines of the part sulphuretted internally. — *Comptes Rendus*, cxxii., p. 312.

PHOTOGRAPHIC PROOFS OBTAINED BY MEANS OF THE X RAYS.

By CH. V. ZENGER.

THE interposition of a plate of wood of several m.m. in thickness prolongs the time of exposure and injures the distinctness of the images by the penumbra which is formed. The defects of the homogeneity of the wood produce streaks in the silhouettes, whilst the use of proofs for surgical diagnosis would require a great precision in the details. I have dispensed with the plate of wood, and I have placed the hand directly on the gelatino-bromide plate, interposing merely a black paper very homogeneous. The image is as definite as possible, and the time of exposure may be reduced to less than an hour.

I have the honour of submitting to the Academy the three following silhouettes:—

1. The hand of my assistant applied on the sensitive plate without anything intervening. The proof shows the bones, the motor muscles, and a gold ring. Time of exposure 45 minutes.

2. A hand into which four fragments of glass had penetrated in the thumb; three of the fragments had been previously extracted, but the fourth is still fixed in the thumb.

3. A hand affected with Morvan's disease. The first joints have already been amputated. We distinguish the progressive destruction of the bones, the parts attacked presenting a greater transparency. Exposure 90 minutes.

I am convinced that the best means of attaining the utmost possible distinctness is to place the sensitive plate in direct contact with the object, and to make use of high tensions so that the Crookes tube may be placed as far as possible without too much prolonging the time of exposure.—*Comptes Rendus*, cxxii., p. 315.

THE PAST, PRESENT, AND FUTURE WATER SUPPLY OF LONDON.*

By E. FRANKLAND, D.C.L., LL.D., F.R.S.

IN a discourse to the members of the Royal Institution on the subject of the Metropolitan water supply nearly thirty years ago, I stated that out of every thousand people existing upon this planet three lived in London; and, as the population of London has in the meantime doubtless grown at a more rapid rate than that of the rest of the world, it will probably be no exaggeration to say that now, out of every thousand people alive on this earth, four live in London; and, therefore, any matter which immediately concerns the health and comfort of this vast mass of humanity may well merit our most earnest attention. Amongst such matters, that of the supply, in sufficient quantity, of palatable and wholesome water is certainly not the least in importance.

It is not, therefore, surprising that this subject has received much attention from several Royal Commissions,

* Condensed report of a Lecture delivered at the Royal Institution, Friday, February 21, 1896.

notably from the Royal Commission on Water Supply of 1867, presided over by the Duke of Richmond; the Royal Commission on River Pollution and Domestic Water Supply of Great Britain, presided over by the late Sir William Denison, of which I had the honour to be a member; and, lastly, that of 1892, of which Lord Balfour of Burleigh was the Chairman.

The Royal Institution has, for nearly three-quarters of a century, been prominently connected with the investigation and improvement of the Metropolitan water supply; no less than four of our Professors of Chemistry have been successively engaged in this work, namely, Professors Brand, Odling, Dewar, and myself; whilst three of them have been members of the Royal Commissions just mentioned. I may, therefore, perhaps be excused for bringing the subject under your notice again for the third time.

On the present occasion, I propose to consider the subject from three points of view, viz., the past, the present, and the future; and, for reasons which will appear hereafter, I shall divide the past from the present at or about the year 1883, and will not go back further than the year 1828, when Dr. Brand, Professor of Chemistry in the Royal Institution, Mr. Telford, the celebrated engineer, and Dr. Roget, Secretary of the Royal Society, were appointed a Royal Commission to enquire into the quality and salubrity of the water supplied to the Metropolis.

The Commissioners made careful examinations and analyses, and reported as follows:—"We are of opinion that the present state of the supply of water to the Metropolis is susceptible of, and requires, improvement; that many of the complaints respecting the quality of the water are well founded; and that it ought to be derived from other sources than those now resorted to, and guarded by such restrictions as shall at all times ensure its cleanliness and purity. (At this time the water was pumped from the Thames between London Bridge and Battersea). To obtain an effective supply of clear water free from insects and all suspended matter, we have taken into consideration various plans of filtering the river water through beds of sand and other materials; and considering this, on many accounts, as a very important object, we are glad to find that it is perfectly possible to filter the whole supply, and this within such limits in point of expense as that no serious objection can be urged against the plan on that score, and with such rapidity as not to interfere with the regularity of the service."

Before the year 1829, therefore, the river water supplied to London was not filtered at all; but after the issue of this report, the companies set themselves earnestly to work to improve the quality of the water by filtration.

In the year 1832, and again in 1849, London was severely visited by epidemic cholera, and the agency of drinking-water in spreading the disease forced itself upon the attention of the observant portion of the medical profession. It was Dr. Snowe, however, who, in August, 1849, first formally enunciated the doctrine that drinking-water polluted by choleraic matters is the chief mode by which cholera is propagated.

In every visitation of Asiatic cholera to London, the water supply was either altogether unfiltered or imperfectly filtered, besides being derived from highly polluted parts of the Thames and Lea; and the enormous loss of life, amounting in the aggregate to nearly thirty-six thousand people, can only be attributed to this cause; for it has now been satisfactorily proved that cholera is, practically, propagated by drinking-water alone; and that efficient filtration is a perfect safeguard against its propagation. Moreover, it is most satisfactory to know that, since the year 1854, no case of Asiatic cholera in London has been traced to the use of filtered river water. The first effect of Dr. Snowe's cardinal discovery was the removal of the intakes of the river water companies to positions beyond the reach of the tide and of the drainage of London. The second was the greater attention paid to the efficiency of filtration.

Such is the verdict with regard to cholera, and the same is true of the other water-borne disease—typhoid fever. But, unlike cholera, this disease is disseminated in several other ways, and its presence or absence in any locality may not of necessity have any connection with drinking-water, as is strikingly shown by the health statistics of Manchester; since the water supply of Manchester, derived as it is from mountain sources, is above all suspicion of this kind. These other causes have, during the last ten years, been much mitigated in London by various sanitary improvements, whilst, as shown in the diagram on the screen, there has been no corresponding mitigation in Manchester. There is no evidence whatever that since the year 1869, when typhoid fever appeared for the first time as a separate disease in the Registrar General's reports, it has been conveyed by the water supply of the Metropolis.

Although very soon after the year 1856 all the water supplied to London was obtained from sources much less exposed to drainage pollution, it was still very carelessly filtered. Previous to the year 1868, there are no records of the efficiency, or otherwise, of the filtration of the Metropolitan water supply derived from rivers; but at that time I began to examine these waters for turbidity. In that year, out of 84 samples, 7 were very turbid, 8 turbid, and 10 slightly turbid; so that, altogether no less than nearly 30 per cent of the samples were those of inefficiently filtered water. The Metropolitan water supply then, up to the year 1868, may be shortly described as derived for many years from very impure sources with either no filtration at all, or with very imperfect filtration; and afterwards, when the impure sources were abandoned, the supply was still often delivered in a very inefficiently filtered condition. But after the establishment of monthly reports, the quality of these waters gradually improved in this most important respect down to the year 1883, since which time the efficiency of filtration of all the river waters supplied to the Metropolis has left little to be desired.

What is it then that separates the past from the present water supply of London? In the first place there is the change of source—I mean the change of the position of the intakes of the several companies drawing from the Thames and Lea, and the total abandonment of the much-polluted Ravensbourne by the Kent Water Company. So long as the water was derived from the tidal reaches of the Thames and Lea, receiving the drainage of an immense population, the risk of infection from water-borne pathogenic organisms could scarcely be otherwise than imminent; for, although we now know efficient filtration to be a perfect safeguard, anything short of efficiency must be attended with risk in the presence of such extreme pollution.

Nevertheless, the line of demarcation between the past and the present water supply of the Metropolis is, in my opinion, to be drawn, not when the intake of the river companies were removed to positions beyond the possibility of pollution by the drainage of London, but it must be drawn at the time when efficient filtration was finally secured and ever since maintained; that is to say, in the year 1884.

The removal of turbidity by sand filtration, however, refers only to suspended matter, but there are sometimes objectionable substances in solution, of which organic matter is the most important. River water and mountain water, even when efficiently filtered, contains more organic matter than spring or deep-well water; but this is reduced in quantity by storage and especially by filtration, although it can perhaps never be brought up to the standard of organic purity of spring and deep well water.

The Present Water Supply.

At present London is supplied with water from four sources—the Thames, the Lea, the New River, and deep wells. Of these, the deep wells yield, as a rule, the purest water, requiring no filtration or treatment of any

kind before delivery for domestic use. The river waters, on the other hand, require some kind of treatment before delivery; storage and subsidence in reservoirs, and filtration. The water from the Thames is abstracted at and beyond Hampton; that from the Lea is taken out at two points, viz., at Angel Road, near Chingford, by the East London Water Company, and above Hertford by the New River Company, who convey it to Green Lanes by an open conduit 25 miles long called the New River Cut, in which it is mixed with a considerable volume of spring and deep well water.

Hitherto I have spoken of chemical purity, or comparative freedom from organic matter, only. But the spread of diseases, such as cholera and typhoid fever, through the agency of drinking-water has no connection whatever with the chemical or organic purity of the water. These diseases are propagated by living organisms of extreme minuteness, to which the names bacilli, bacteria, microbes, and others have been given; and here comes the important question—How does filtration secure immunity from these water-borne diseases?

To Dr. Koch, of Berlin, we are indebted for the answer to this question. By his discovery of a means of isolating and counting the number of microbes and their spores in a given volume of water we were, for the first time, put into possession of a method by which the condition of water as regards these living organisms, before and after filtration, could be determined with quantitative exactness. The enormous importance of this invention, which was first made known and practised in England in 1882 by the late Dr. Angus Smith, is evident when it is borne in mind that the living organisms, harmful or harmless, contained in water are of such extreme minuteness as practically to defy detection by ordinary microscopical examination. But, although the microscope cannot detect with certainty single bacteria or their spores, even the naked eye can easily discern towns or colonies consisting of thousands or even millions of such inhabitants.

Dr. Koch's method accomplishes at once two things—it isolates, in the first place, each individual microbe or germ; and, secondly, places it in conditions favourable for its multiplication, which takes place with such amazing rapidity that even in a few hours, or at most in two or three days, each organism will have created around itself a visible colony of innumerable members—a town, in fact, comparable to London itself for population. By operating upon a known volume of water, such as a cubic centimetre, for instance, the number of separate organisms or their spores in a given volume of the water under investigation can thus be determined.

In order to ascertain the effect of filtration upon the bacterial quality of the water, it is absolutely necessary that the sample should be taken immediately after it has passed through the sand filters; for if it be obtained from the delivery mains in town—that is to say, after the water has passed through many miles of pipes—the rapid multiplication of these organisms, except in very cold weather, is such that a water which contains only a single living organism per c.c. as it issues from the filter, may contain 100 or 1000 in the same volume when, after several hours, it arrives at the consumer's premises.

Now, what is the effect of sand filtration as carried out by the various water companies supplying London upon the living matter contained in the raw river water? It is simply astounding. Water which is poured upon sand filters containing thousands of bacteria per c.c.—for a single drop of Thames water sometimes contains 3000 separate living organisms—comes out from those filters with 50, 30, 10, or even less of these organisms per c.c., or the number of microbes in a single drop is reduced to 2, or even none.

Rather less than one-tenth of the total volume of water supplied to London is derived by the Kent Water Company from deep wells in the chalk. As it issues from the porous rock into the fissures and headings of these

wells, this water is, in all probability, absolutely sterile; but by the time it has been pumped up to the surface, it usually contains a small number of microbes. Thus, during the year 1892 it contained, on the average, 6 per c.c.; in 1893, 13; in 1894, 15; and in 1895, 8.

Thus, although the deep well water has, from a bacterial point of view, a decided advantage, the filtered river waters are not very far behind, and there is every reason to believe that, with the improvements that are now being carried out by the various river water companies, the Kent Company's water will before long, be run very hard by the other supplies.

By the examination of the water as it issues from the filters, the utmost freedom from microbes, or maximum degree of sterility, of each sample is determined. This utmost freedom from bacterial life, after all sources of contamination have been passed, is obviously the most important moment in the history of the water, for the smaller the number of microbes found in a given volume at that moment, the less is the probability of pathogenic organisms being present; and, although the non-pathogenic organisms may afterwards multiply indefinitely, this is of no consequence in the primary absence of the pathogenic. But it is only fair in describing the character of the present water supply of London to say that not a single pathogenic organism has ever been discovered, even in the unfiltered water as it enters the intakes of the various companies, although these organisms have been diligently sought for. It is sometimes even said that the non-pathogenic organisms found in water may be beneficial to man, but this idea is not borne out by their entire absence from the food which Nature provides for young animals; milk is absolutely sterile, if healthy.

As it is at present impracticable to obtain water, uniformly at least, free from microbes, it is desirable to adopt some standard of bacterial purity, and 100 microbes per c.c. has been fixed upon, by Dr. Koch and myself, as the maximum number allowable in potable water. This standard is very rarely infringed by the London water companies, whilst I have every reason to hope that in the near future, now that special attention is directed to bacterial filtration, it will not be approached within 50 per cent. This hope is based, not only upon my own observations, but also upon the exhaustive and important investigations carried out at the Lawrence Experiment Station by the State Board of Health of Massachusetts under the direction of Mr. George W. Fuller, the Official Biologist to the Board. More than six years have already been spent in the prosecution of these American experiments, and many thousands of samples of water have been submitted to bacterial cultivation.

These important experiments, and my own observations on the London waters continued for four years, lead to the following conclusions:—

1. The rate of filtration between half a million and three million gallons per acre per day exercises practically no effect on the bacterial purity of the filtered water. It is worthy of note that the rates of filtration practised by the several water companies drawing their supplies from the Thames and Lea are as follows:—Chelsea Company, 1,830,000; West Middlesex, 1,359,072; Southwark Company, 1,568,160; Grand Junction Company, 1,986,336; Lambeth Company, 1,477,688; New River, 1,881,792; and East London, 1,393,920. Hence, not one of the London companies filters at the rate of two million gallons per acre per day; at which rate, in the Massachusetts filters, 99.9 per cent of the microbes present in the raw water were removed.

2. The effect of the size of sand grains used in the filters is very considerable. Thus, by the use of a finer sand than that employed by the Chelsea Company, the West Middlesex Company is able, with much less storage, to attain an equal degree of bacterial efficiency.

3. The depth of sand, between the limits of 1 and 5 ft., exercises no practical effect upon bacterial purity when

the rate of filtration is kept within the limits just specified. Thus, the New River Company, with 1·8 ft. of sand on their filters, compares favourably with the Chelsea Company, the sand on whose filters is more than twice that depth. Placed in the order of thickness of sand on their filters, the Metropolitan companies range as follows:—Chelsea, Lambeth, West Middlesex, Southwark, East London, Grand Junction, and New River. Placed in the order of efficient bacterial filtration, they range as follows:—Chelsea and West Middlesex equal, New River, Lambeth, East London, Southwark, and Grand Junction.

4. When there is such an accumulation of deposit on the surface of a sand filter that, for practical purposes, sufficient water cannot be made to pass through it, the surface of the filter has to be scraped; that is to say, mud and about half an inch of the sand are removed from the surface. After this operation there is often an increase in the number of bacteria in the filtered water, and it has been noticed that the increase is greater in shallow than in deep filters, and with high than with low rates of filtration; and there is no doubt that the effect of scraping is considerably magnified when the coarser descriptions of sand are employed, as is the case in the filters of the London water companies. I should, therefore, like to impress upon the engineers of these companies the desirability of using finer sands than are at present employed.

The lecturer here described a long series of experiments proving that the temperature of the water and the presence or absence of sunshine has little or no effect upon the number of microbes in river water, whilst the presence of flood water is almost invariably accompanied by an enormous increase in the number of microbes, showing that the microbial population of a river is directly dependent upon the volume of water flowing in its bed.

The Water Supply of the Future.

In view of the rapid increase of the population of London, fears have from time to time been entertained that the water supply from the Thames basin—that is to say, from the rivers Thames and Lea supplemented by water from springs and deep wells within the basin itself—would soon be insufficient in quantity; whilst the quality of the water taken from the river has, up to comparatively recent date, been considered unsatisfactory. On these grounds, various schemes have from time to time been brought forward for the supply of the Metropolis from other river basins: from the Wye, the Severn, the river basins of North Wales, and of the Lake Districts of Cumberland and Westmoreland. It is worthy of note, however, that all the Royal Commissions have arrived unanimously at the conclusion that the quantity of water obtainable from the Thames basin is so ample as to render the necessity of going elsewhere a very remote contingency.

I shall now endeavour to put, very shortly, before you the facts which, in my opinion, prove that, both as regards quantity and quality, the Thames basin will, for a very long time to come, afford an abundant supply for the Metropolis. There is, indeed, no river basin in Great Britain which affords such an abundant supply of excellent water as that available in the Thames basin. Besides that which flows directly into the rivers, this water is contained in the chalk, oolite, and lower greensand, which are the best water-bearing strata in the kingdom. From these strata it issues in copious springs of unsurpassed organic purity. For dietetic purposes there is no better water in the kingdom than the underground water of the Thames basin. For sentimental reasons, I should like to see it conveyed to the works of the various companies in special conduits, but we have seen that, on hygienic grounds, it may safely be allowed to flow down the bed of the Thames if it be afterwards efficiently filtered.

So much for quality, now as to quantity. The basins of the Thames and Lea include an area of upwards of five

thousand square miles. Of this, more than one-half, including the oolitic, cretaceous, and portions of the tertiary formations, is covered by a porous soil upon a permeable water-bearing stratum. The remainder is occupied by the Oxford, Kimmeridge, Gault, and London Clay; being thus covered by a clay soil upon a stiff and impervious subsoil. The annual rainfall of the district averages 28 inches. The rivulets and streams of the Thames basin are formed and pursue their course on the clay land. There are no streams on the chalk. That which falls upon the porous stratum and does not evaporate sinks, mostly where it alights, and heaps itself up in the water-bearing stratum below, until the latter can hold no more. The water then escapes as springs at the lowest available points. Innumerable examples of these springs occur all round the edge of the Thames basin, and at various points within it. Thus, from the chalk they are ejected at the lip of the gault, and in the oolitic area by the Fuller's earth below it, or by the Oxford clay, geologically, above it.

According to the gaugings of the engineer of the Thames Conservancy Board, there passed over Teddington Weir in 1892 387,000 millions of gallons, equal to an average flow of 1060 millions daily. In the following year, 1893, there passed over this weir an aggregate of 324,227 millions of gallons, or a daily average of 888 millions of gallons; the average for the two years being 974 millions of gallons, and this number does not include 120 millions of gallons daily abstracted by the five London water companies who draw their supplies from the Thames. Thus, in round numbers, we may say that, after the present wants of London have been supplied from this river, there is a daily average of nearly a thousand millions of gallons to spare. Surely it is not too violent an assumption to make that the enterprising engineers of this country can find the means of abstracting and storing, for the necessary time, one-fourth of this volume.

As regards the quality of this stored water, all my examinations of the effect of storage upon the chemical, and especially upon the bacterial, quality point to the conclusion that it would be excellent; indeed, the bacterial improvement of river water by storage for even a few days is beyond all expectation. Thus, the storage of the Thames water by the Chelsea Company for only thirteen days reduces the number of microbes to one-fifth of the original amount, and the storage of the river Lea water for fifteen days by the East London Company reduces the number, on the average, from 13,693 to 2752 per c.c., or to one-fifth. Indeed, quietness in a subsidence reservoir is, very curiously, far more fatal to bacterial life than the most violent agitation in contact with atmospheric air; for the microbes which are sent into the river above the falls of Niagara by the City of Buffalo seem to take little or no harm from that tremendous leap and turmoil of waters, whilst they subsequently, very soon, almost entirely disappear in Lake Ontario. Thus, it is not too much to expect that storage, say, for a couple of months, would reduce the number of microbes in Thames flood water down to nearly the minimum ever found in that river in dry weather; whilst, by avoiding the first rush of each flood, a good chemical quality would also be secured. There is, therefore, I think, a fair prospect that the quantity of water derivable from the Thames at Hampton could be increased from its present amount (120 millions of gallons per diem) to 370 millions.

Again, in the river Lea, although here the necessary data for exact calculation are wanting, it may be assumed that the present supply of 54 millions of gallons could be increased by the storage of flood water to 100 millions of gallons per day. To these volumes must be added the amount of deep well water which is obtainable from those parts of the Thames basin which lie below Teddington Lock, and in the Lea basin below Lea Bridge, and which was estimated by the last Royal Commission at rather more than 67½ millions of gallons. Thus we get the

grand total of 537½ millions of gallons of excellent water obtainable within the Thames basin, the quality of which can be gradually improved, if it be considered necessary, by pumping from the water-bearing strata above Teddington and Lea Bridge respectively, instead of taking the total supply from the open rivers above these points. Such a volume of water would scarcely be required for the supply of the whole water area of London at the end of fifty years from the present time, even supposing the population to go on increasing at the same rate as it did in the decade 1881—91, which is an assumption scarcely likely to be verified.

In conclusion, I have shown that the Thames basin can furnish an ample supply for fifty or more years to come; whilst the quality of the spring and deep well water and the efficiently filtered river water would be unimpeachable. To secure these benefits for the future, storage must be gradually provided for 11,500 millions of gallons of flood water, judiciously selected, in the Thames valley, and a proportionate volume in the basin of the Lea; whilst filtration must be carried to its utmost perfection by the use of finer sand than is at present employed, and by the maintenance of a uniform rate during the twenty-four hours.

The lecturer concluded as follows:—There is nothing heroic in laying pipes along the banks of the Thames or even in making reservoirs in the Thames basin; they do not appeal to the imagination like that colossal work—the bringing of water to Birmingham from the mountains of Wales; and there is little in such a scheme to recommend it to the mind of the enterprising engineers of to-day. Nevertheless, by means of storage, by utilising springs, by sinking deep wells, and by such comparatively simple means, we have, in my opinion, every reason to congratulate ourselves that, for half a century at least, we have at our doors, so to speak, an ample supply of water which, for palatability, wholesomeness, and general excellence, will not be surpassed by any supply in the world.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 6th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MR. J. T. DUNN was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Sidney Barwise, The Lindens, Derby; Ernest Hunter Fisher, The County Laboratory, St. Albans; William Henry Merrett, Lambeth Brass and Iron Works, Short Street, Lambeth, S.E.; Joseph W. Patterson, Esq., Avenue Road, West Hartlepool; H. von Pechmann, Tübingen, Germany; James Proude, 13, Oak Terrace, Halifax; Henry Renney, M.D., B.Sc., D.P.H., Durham, Brookfield House, Durham Road, Sunderland; Henry Fishwick Robinson, B.Sc., Sparthfield, Droylsden Road, Newton Heath, Manchester; John Henry Wolfenden, 226, Ashton Road, Failsworth, Manchester.

Of the following papers those marked * were read:—

*12. "The Molecular Weight and Formula of Phosphoric Anhydride and of Metaphosphoric Acid." By W. A. TILDEN and R. E. BARNETT.

The molecular formulæ As_4O_6 , Sb_4O_6 , P_4O_6 , $P_4O_6S_4$, and P_4S_6 , have been already established by determinations of the vapour densities of these compounds. The formula P_2O_4 has been assigned by Thorpe and Tutton to the compound they designate as phosphorus tetroxide, but no determination of the vapour density having been attempted it remains uncertain whether this formula truly expresses the molecular weight. The authors are of opinion that the low vapour density observed by V. and

C. Meyer in the case of phosphoric sulphide is due to dissociation of that compound on vaporisation into phosphorus sulphide and sulphur.

They have made a series of determinations of the density of the vapour of phosphoric anhydride at a bright red heat with results which point to the formula P_4O_{10} , instead of the simpler expression P_2O_5 , which has always hitherto been accepted, chiefly on the ground of its assumed analogy with the pentasulphide.

They have also made determinations of the density of the vapour of metaphosphoric acid, from which they draw the conclusion that this compound is partly dissociated by heat into water and the anhydride, and that the acid must be represented by the molecular formula $H_2P_2O_6$.

DISCUSSION.

Mr. DAVID HOWARD remarked that distilled metaphosphoric acid had been known commercially.

Professor THORPE observed that in the course of his work with Mr. Tutton on phosphorous oxide, he had noticed the volatility of phosphorus pentoxide, but had not been able to make use of the property, owing to the readiness with which glass was attacked by the heated substance. He agreed with the authors in believing that phosphorus pentasulphide dissociates when it volatilises, and that on this account the molecular formula P_2S_5 was open to doubt. He also concurred as to the desirability of re-determining the formulæ of many of the metallic metaphosphates.

*13. "Lead Tetracetate and the Plumbic Salts." By A. HUTCHINSON, M.A., Ph.D., and W. POLLARD, B.A., Ph.D.

In September, 1893, the authors communicated to the Society a short note on lead tetracetate (*Trans.*, lxiii., 1136). Since that date the work has been extended, and the detailed results are contained in the present paper.

Lead tetracetate is obtained when red lead is dissolved in glacial acetic acid, and crystallises from the solution in monosymmetric needles, $a : b : c = 0.5874 : 1 : 0.48485$. $\beta = 74^\circ 24'$.

The specific gravity of the crystals is 2.28; they are readily soluble in chloroform and hot acetic acid, and the molecular weight determined in the latter solvent is 365 by the boiling-point method, and 408 by the freezing-point method. Lead tetracetate is decomposed by water with extraordinary ease into lead dioxide and acetic acid; acted upon by gaseous hydrogen chloride it yields lead tetrachloride, whilst if dissolved in aqueous hydrogen chloride and the solution added to a solution of ammonium chloride, the double salt, $(NH_4)_2PbCl_6$, is precipitated. When acted upon by orthophosphoric acid, lead tetracetate yields a tetraphosphate, to which the formula $Pb(HPO_4)_2$ is probably to be assigned; a propionate, $Pb(C_3H_5O_2)_4$, analogous to the tetracetate, has been prepared.

The authors point out that thallic and manganic acetates, with properties very similar to those of lead tetracetate, have been described, and give a list of salts of tetravalent lead, owing to the close analogies which exist between the stannic salts and the salts of tetravalent lead. The authors propose that the latter should be termed plumbic salts.

*14. "An Improved Method of Determining Urea by the Hypobromite Process." By ALFRED H. ALLEN.

It is well known that in the ordinary way of employing the hypobromite process for the determination of urea, the evolution of nitrogen in the form of gas is only about 92 per cent of the total nitrogen present. An increased yield of nitrogen is obtainable by adding glucose, and by certain other devices, but these modifications are open to several objections, and have not met with general acceptance.

In a paper recently read before the Society (*Trans.*, lxvii., 746), Messrs. Walker and Hambly described some suggestive experiments on the transformation of ammonium cyanate into urea. They find that the reaction is

never complete, and they further point out that the reverse reaction occurs when an aqueous solution of urea is boiled. It follows that a solution containing both ammonium cyanate and urea ultimately arrives at a condition of equilibrium, which is upset if ammonium sulphate or potassium cyanate be added to the solution, the urea in each case being rendered more stable.

From these results it appeared probable that the incomplete evolution of nitrogen in the hypobromite process of determining urea might be due to a reversion of a portion of the urea to the condition of cyanate, especially as H. J. H. Fenton had shown (*Trans.*, xxxiii., 300) that cyanate was a product of the reaction of alkaline hypochlorites on urea, and W. Foster (*Trans.*, xxxv., 122) made the same observation with alkaline hypobromite. Fenton also found that cyanates evolved no gas when treated with alkaline hypobromite, and the author can confirm this observation. Hence it appeared possible that, by adding a sufficiency of potassium cyanate to the urea solution before adding the hypobromite, the reversion of the urea to cyanate might be entirely prevented. Experiment has proved this conjecture to be correct. An addition of 0.250 grm. of pure potassium cyanate to the solution of 0.100 grm. of urea in 5 c.c. of water, raised the evolved nitrogen from 91 to nearly 97 per cent (corr.).

If the ordinary method of operating be reversed, and instead of adding the urea solution (mixed with potassium cyanate) to a highly alkaline solution of sodium hypobromite, the cyanate be added to the solution of urea, followed by caustic soda when its solution is complete, and the bromine solution be then gradually run in, still better results are obtained. Under these conditions the yield of nitrogen is from 99.8 to 100.0 per cent (corr.). Hence the addition of potassium cyanate to the extent of two to three times the weight of the urea present effects a complete evolution of the nitrogen in the form of gas, and prevents the irregularities and uncertainty attaching to the hypobromite process in its ordinary form.

The idea of reversing the usual mode of procedure appears to have originated with J. R. Duggan (*Amer. Chem. Journ.*, iv., 47), who states that fully 99 per cent of the ureal nitrogen is evolved as gas if 5 c.c. of urine be first mixed with 20 c.c. of a solution of 20 grms. of caustic soda in 100 c.c. of water, and 1 c.c. of bromine be gradually added. I have not been able to obtain so high a yield as 99 per cent of gas without the addition of potassium cyanate, but the reversed process is in any case a valuable improvement on the ordinary method of working.

A convenient arrangement for the reversed form of the process is found in the author's work on the "Chemistry of Urine." In this apparatus a separatory funnel is substituted for the sample-tube generally used. Five c. c. of the urine or other solution of urea should be placed in the flask, and 0.250 grm. of potassium cyanate added. When solution is complete, 25 c.c. of a 40 per cent aqueous solution of caustic soda is added, the separator adjusted, and the flask connected to the nitrometer. A solution of 2 c.c. of bromine in 16 c.c. of a 20 per cent aqueous solution of potassium bromide is then added gradually from the tapped separator. The evolution of nitrogen occurs very promptly, and is usually complete by the time one-half of the prescribed volume of bromine solution has been added.

The use of silver cyanate, with or without simultaneous addition of sodium chloride, was found less satisfactory than the addition of the potassium salt.

It appeared probable that the reaction of the alkaline hypobromite with potassium cyanide would result in the formation of cyanate, in which case potassium cyanate could be conveniently extemporised in the liquid. Experiment showed that, on adding potassium cyanide to the alkaline hypobromite, great evolution of heat occurred, cyanate is formed, but the reaction appears to be complex, and the product had not the same effect as previously prepared potassium cyanate. The author intends to in-

vestigate this reaction more completely, as it does not appear to have been previously studied.

DISCUSSION.

Mr. FENTON made an experiment to show that when sodium hypochlorite reacts with urea the quantity of nitrogen evolved is only one-half of that obtained by the action of hypobromite. He had been unable to find an entirely satisfactory explanation of the fact.

Professor THORPE pointed out that Lord Rayleigh had stated that the gas evolved by the reaction of urea with alkaline hypobromite was not pure nitrogen, and suggested the desirability of examining the gas more fully.

Professor TILDEN concurred in regarding this as an important point.

Mr. HEHNER thought Mr. Allen's modified method of using this alkaline hypobromite would prove of value. He did not consider, however, that the mode of action of the potassium cyanate had been completely explained.

Mr. GROVES and Mr. PAGE remarked that the simplicity and rapidity of the hypobromite method was a strong recommendation from the clinical point of view; and Mr. PAGE pointed out that the employment of free bromine, which is required for the "reversed" process, would be a disadvantage in the wards of a hospital.

Mr. CROSS thought if would be of interest in connection with the anomalous behaviour of urea to mention that he had observed that, whilst a mixture of sulphuric acid and potassium dichromate failed to cause the evolution of nitrogen from urea, this gas is plentifully evolved if a nitrate is added to the mixture.

*15. "Preliminary Note on the Absorption of Moisture by Deliquescent Salts." By H. WILSON HAKE, Ph.D.

Some years ago the author, in experimenting with deliquescent salts, found that they exerted a desiccating action on other deliquescent salts, indicating a difference in the degree of attraction for moisture on the part of such salts.

More recently experiments were commenced with the intention of measuring, if possible, the relative degree of deliquescence, or specific deliquescence, of certain salts.

On exposing known quantities to the air, and weighing them at frequent intervals, in all cases, without exception, a maximum of deliquescence was reached in a few days, and from this point a gradual decline in weight almost invariably followed.

This maximum coincides with the formation of a definite hydrate, in a large number of cases, when the salt was pure; the water contained in it at its maximum of deliquescence approximately coincides with that required for a definite number of water molecules. As in all such cases, there was a possible margin of 1 per cent and over for the next one molecule more or less of water, the author concludes that the phenomenon of deliquescence in certain salts, and possibly other substances, is due to a tendency on their part to form a definite hydrate.

The accompanying table indicates some of the results obtained at present (see next page).

The above salts were found to be practically pure on analysis; with less pure salts an approximation to a definite hydrate was obtained, but in most cases this was sufficiently close to indicate the probable truth of the hydrate assumption.

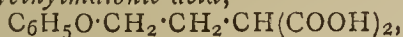
DISCUSSION.

The PRESIDENT, Professor E. W. MORLEY, and Professor DUNSTAN commented on the fact that Dr. Hake had not so far studied the relation of the amount of absorption to the vapour pressure of water in the atmosphere to which the salts were exposed, and pointed out that until this had been done no positive conclusion could be drawn from the results.

16. "Some Derivatives of γ -Phenoxyethylmalonic Acid and of γ -Phenoxyethylacetic Acid," By W. H. BENTLEY, E. HAWORTH, and W. H. PERKIN, jun.

A.	B.	C.	D.	E.	F.	G.	H.
Substance.	Original hydration per cent.	Maximum hydration per cent reached.	Nearest molecular formula corresponding to C.	Theoretical hydration per cent corresponding to D.	Difference between theoretical and found hydration per cent.	Theoretical difference per cent for 1 mol. H ₂ O more than D.	Theoretical difference per cent for 1 mol. H ₂ O less than D.
MgCl ₂ 6H ₂ O ..	53.20	77.20	MgCl ₂ 18H ₂ O	77.33	-0.13	+0.93	-1.02
Mg(NO ₃) ₂ 4H ₂ O ..	18.18	65.89	Mg(NO ₃) ₂ 16H ₂ O	66.05	-0.16	+1.35	-1.46
CaCl ₂ 6H ₂ O ..	49.31	73.24	CaCl ₂ 17H ₂ O	73.38	-0.14	+1.10	-1.20
Fe ₂ Cl ₆ 12H ₂ O ..	39.92	66.52	Fe ₂ Cl ₆ 36H ₂ O	66.59	-0.07	+0.61	-0.63
NiCl ₂ 6H ₂ O ..	45.38	70.03	NiCl ₂ 17H ₂ O	70.18	-0.15	+1.18	-1.28
Mn(NO ₃) ₂ 3H ₂ O ..	23.17	61.54	Mn(NO ₃) ₂ 16H ₂ O	61.67	-0.13	+1.42	-1.54
H ₂ PtCl ₆ 6H ₂ O ..	20.85	47.82	H ₂ PtCl ₆ 21H ₂ O	47.97	-0.15	+1.16	-1.22
H ₂ SO ₄	4.20	64.63	H ₂ SO ₄ 10H ₂ O	64.74	-0.11	+2.15	-2.43
LiCl	0.00	77.40	LiCl8H ₂ O	77.21	+0.19	+2.00	-2.44

γ-Phenoxyethylmalonic acid,



is easily prepared by the action of $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, β -bromethylphenyl ether, on ethylic sodiomalonate, and the hydrolysis of the resulting ethereal salt with potash. It crystallises from xylene in minute needles melting at 142° with slight evolution of gas.

γ-Phenoxybutyric acid, $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, *γ-phenoxyethylacetic acid*, is obtained by heating *γ-phenoxyethylmalonic acid* to 160 — 200° until the evolution of carbon dioxide ceases. It separates from light petroleum in thin plates melting at 64 — 65° . Heated with fuming hydrobromic acid it loses phenol, forming a bromo-derivative, which, on boiling with sodium carbonate and acidifying the product, yields butyrolactone.

Diphenoxyethylmalonic acid,—



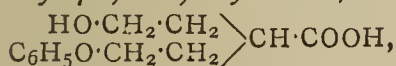
is obtained by acting on ethylic malonate twice with sodium and β -bromethylphenyl ether, and subsequent hydrolysis of the product with potash. It crystallises from 50 per cent acetic acid in prisms melting at 150° with decomposition.

Diphenoxyethylacetic acid,—



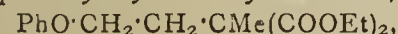
is prepared by heating diphenoxyethylmalonic acid at 180° until carbon dioxide ceases to be evolved. It separates from light petroleum in needles melting at 88° .

α-Phenoxyethyl-γ-hydroxybutyric acid,—



results on heating diphenoxyethylacetic acid with hydrogen chloride, dissolved in acetic acid for some hours at 130° . It crystallises from benzene in plates melting at 112° , and is very sparingly soluble in ether.

Ethyl-γ-phenoxyethyl-α-methyl malonate,—

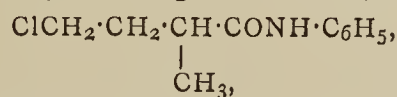


is prepared by the action of $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Br}$ on the sodium compound of ethylic methyl malonate. It is a thick, colourless oil (b. p. 230° , pressure 45 m.m.), which, on hydrolysis, gives the corresponding dibasic acid *γ-phenoxyethyl-α-methylmalonic acid*. This acid crystallises from benzene in colourless prisms, which melt at 125°C .

γ-Phenoxy-ethyl-α-methylacetic acid is obtained by heating the previous acid at 180° till evolution of CO_2 ceases, and then distilling in a vacuum (b. p. 207° , pressure 45 m.m.). Re-crystallised from light petroleum, the acid melts at 80° . This acid was also obtained by the action of β -bromethylphenyl ether on the sodium compound of ethylic methylacetoacetate, and saponifying the resulting ether (a colourless syrup, b. p. 185° , pressure 40 m.m.) with strong alcoholic potash.

α-Methylbutyrolactone was obtained from the previous acid by first treating with aqueous hydrobromic acid, and then boiling the resulting bromo-acid with sodium carbonate solution.

The lactone was then re-converted into *γ*-bromethyl- α methylacetic acid by treatment with HBr. This acid, which is very unstable, is a brownish, oily substance; its ethyl ether is also unstable, and could not be distilled. *γ*-Chlorethyl- α -methyl acetyl chloride was obtained as a colourless liquid (b. p. 189°) by the action of phosphorus pentachloride on α -methylbutyrolactone. This chloride, when acted on by aniline, gave an anilide,—



which crystallises from light petroleum in colourless prisms (m. p. 106°).

17. "Note on the Preparation of Glycol." By E. HAWORTH and W. H. PERKIN, jun.

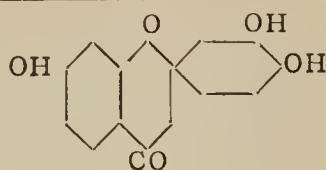
This paper describes a modification of the usual method of preparation of glycol, which consists in decomposing in a given volume of aqueous potassium carbonate, successive quantities of ethylene dibromide, by which means a concentrated solution of glycol is obtained, and subsequent loss by evaporation is reduced to a minimum.

18. "Luteolin." By A. G. PERKIN.

Luteolin, the yellow colouring-matter of Weld (*Reseda luteola*), was first isolated by Chevreul (*J. Chim. Méd.*, vi., 157), and has been subsequently investigated by others. The formula $\text{C}_{20}\text{H}_{14}\text{O}_8$ was assigned to it by Moldenhauer, $\text{C}_{12}\text{H}_8\text{O}_5$ by Schützenberger and Paraf, and $\text{C}_{15}\text{H}_{10}\text{O}_6$ by Hlasiwetz and Pfandler. The results here obtained agree with $\text{C}_{20}\text{H}_{14}\text{O}_8$ and $\text{C}_{15}\text{H}_{10}\text{O}_6$, and that the latter is correct is proved by the production of various derivatives. In a similar manner to quercetin, fisetin, and morin (*Trans.*, 1895, 644), luteolin combines with mineral acids, yielding the crystalline compounds $\text{C}_{15}\text{H}_{10}\text{O}_6\text{H}_2\text{SO}_4$, $\text{C}_{15}\text{H}_{10}\text{O}_6\text{HBr}\cdot\text{H}_2\text{O}$ and—



which, in contact with water, are decomposed into luteolin and the free acid. Luteolin yields a tetracetyl compound, $\text{C}_{15}\text{H}_6\text{O}_6(\text{C}_2\text{H}_3\text{O})_4$, colourless needles, m. p. 213 — 215° , a tetrabenzoyl compound, $\text{C}_{15}\text{H}_6\text{O}_6(\text{C}_7\text{H}_5\text{O})_4$, m. p. 200 — 201° , and a dibromo-compound, $\text{C}_{15}\text{H}_8\text{Br}_2\text{O}_6$, yellow needles, m. p. 303° . The acetyl compound of this latter, $\text{C}_{15}\text{H}_4\text{Br}_2\text{O}_6(\text{C}_2\text{H}_3\text{O})_4$, melts at 218 — 220° . Rochleder has previously found that luteolin, by fusion with alkali, yields phloroglucin and protocatechuic acid, but preliminary experiments have shown that though the former is so produced, the presence of the latter could not be detected. There was, however, isolated a second substance in the form of nearly colourless needles, melting at 210° , but giving no colouration with ferric chloride. On methylation, luteolin yields a compound of the formula $\text{C}_{15}\text{H}_6\text{O}_6(\text{CH}_3)_4$, m. p. 191 — 192° . It is considered probable that luteolin is very similarly constituted to fisetin, $\text{C}_{15}\text{H}_{10}\text{O}_6$, or tetrahydroxy- β -phenyl- γ -pyron, Herzig (*Ber.*, 1895, xxviii., 293),—



which it very closely resembles.

19. "An Examination of the Products obtained by the Dry Distillation of Bran with Lime." By W. F. LAYCOCK, Ph.D.

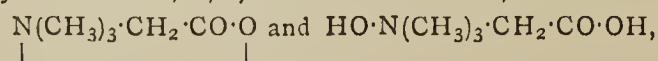
Considerable quantities of bran and unslaked lime, in the proportions of 1 : 2 by weight, were subjected to dry distillation. The resulting distillate consisted of a black oil floating on an aqueous solution. The solution contained considerable quantities of ammonia, chiefly as bicarbonate, also amines and pyrrols, together with small amounts of ketones, and ethyl alcohol.

The oil, after re-distilling, was treated with dilute hydrochloric acid, and the pyridine bases thus separated were afterwards purified. The unchanged oil was freed from small amounts of ketones by shaking with sodium bisulphite solution. The residual oil consisted of a mixture of hydrocarbons and pyrrol homologues with small quantities of furfuranes and indole.

20. "Constitution of Glycocine." By JOJI SAKURAI.

Since the publication of my paper on the "Constitution of Glycocine and its Derivatives" (*Proc. Chem. Soc.*, 137), important facts have been contributed to the history of the subject by eminent authorities, and it is interesting to observe that these new facts are either confirmatory of the ring constitution or, at least, in conformity with it.

Walker (*Proc. Chem. Soc.*, 137) has made the very important observation that glycocine is virtually a non-conductor of electricity, whilst phenylglycocine, hippuric acid, and aceturic acid are far better conductors than acetic acid, and has concluded that these glycocine derivatives must be open-chain compounds, and that, by analogy, glycocine itself has not the ring constitution. But if electric conductivity of glycocines proves anything as to their constitution it must be concluded, by the very same reasoning, that glycocine itself, being a non-conductor, cannot be an open-chain compound. A probable explanation of the difference in the electric conductivities of glycocine and its derivatives, which gives every support to the view of the cyclic constitution of the glycocines, seems obvious to me. It is that while glycocine itself appears not to form an addition compound when dissolved and, consequently, could undergo no ionisation, its derivatives do form such addition compounds, these being, as pointed out in my paper, open-chain compounds, and, therefore, capable of more or less ionisation. Betaine is an example in point which, in the anhydrous and hydrated states, is, by universal admission,—



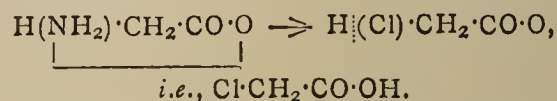
respectively.

Tilden and Forster (*Trans.*, lxvii., 489; *Proc.*, 151) find that the primary action of nitrosyl chloride upon glycocine and several of the acid-amides is to replace the NH_2 -group by Cl; glycocine, in this manner, producing chloracetic acid. This fact they consider to be at variance with the ring formula of glycocine. The difficulty, however, does not exist. There being, as they say, complete removal of the NH_3 -group by NOCl with formation of N_2 , H_2O , and HCl , the remaining group will be $\text{CH}_2 \cdot \text{CO} \cdot \text{O}$,

and this, like ethylene oxide, will almost inevitably combine with hydrogen chloride, and produce chloracetic acid. This explanation is in conformity with that which Tilden and Forster give of the production of acetic acid from acetamide, where they assume that acetyl chloride is first formed, and then acted upon by water.

The ring formula of glycocine gives yet another explanation of the formation of chloracetic acid, and again

from Tilden and Forster's standpoint. Admitting, as they say, that by the action of nitrosyl chloride there is an interchange between NH_2 and Cl, of the divalent group, NH_3 , there will be H left along with the Cl, but hydrogen and chlorine being both monovalent, the H will go to the half-freed O, so as to give rise to chloracetic acid.



These two explanations of the production of chloracetic acid from glycocine differ only in assuming or not that hydrochloric acid has a temporary existence apart from the rest of the elements prior to the formation of chloracetic acid.

A full account of the facts supporting the theory that the glycocines are closed chain compounds is contained in the *Journal of the College of Science, Imp. Univ., Japan.*

NOTICES OF BOOKS.

Kelly's London Medical Directory, 1896, London: Kelly and Co., Limited. Pp. 519.

THE utility of this volume is not limited to the medical profession. It begins with a list of the examining bodies of London. Of these, first and foremost stands the London University, which we are duly reminded is not a teaching or still less a researching body. We hope the time may come when it may have to hand over its proud name to an organisation whose object shall be neither political nor denominational, but purely scientific.

The Local Government Board has a curious organisation. It has a staff of engineering inspectors of whom six are military men, and only three civilians. There is also a body of medical inspectors, but no chemical inspectors save the inspectors under the Alkali Acts, who, fortunately, are not soldiers.

Of course we do not censure Kelly's Directory for such a transgression against common sense. It can merely put on record facts as they exist, and leave its readers to draw the needful conclusions.

We are glad to find here the address of the Association for the Advancement of Medicine by Research,—i.e., 57, Wimpole Street. This Society is an attempt at a Biological Research Defence League, but it is deficient in confining its endeavours to medical research, and by a policy of "masterly inactivity" strikingly in contrast to that of the "anti" societies against which it should combat. We are happy to find that societies of that class are not honoured by a mention in this Directory.

In the main portion of the work before us, which gives the names and addresses of legitimate medical practitioners in London and its district, we find what to us appears a needless prolixity. Attached to many names of physicians and surgeons we find not only the degrees which they have taken, the learned societies to which they belong, and the works which they have written, but communications which they have addressed to various journals, and the names of ships on which they have sailed in their professional capacity.

It is highly desirable that ships' surgeons should be appointed not by the owners of the vessels, but by a national authority. At present the more thoroughly a ship's surgeon does his duty, the more doubtful is his term of office.

In the street directory, N. district, we see an omission of Tollington Park, in which several qualified practitioners reside.

Among the hospitals we are not able to find that for fevers in Liverpool Road, Islington.

Altogether, "Kelly's Medical Directory" will be found very widely useful.

Computation Rules and Logarithms, with Tables for other Useful Functions. By SILAS W. HOLMAN, Professor of Physics at the Massachusetts Institute of Technology. New York and London: Macmillan and Co. 1896. Pp. 73.

THIS work contains tables of logarithms to four and five places, besides square roots and squares, four place reciprocals, slide wire ratios, natural sines and cosines, natural tangents and cotangents, all four place, besides five place logarithms of sines, cosines, tangents and cotangents, and certain useful constants.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 5, February 3, 1896.

Observations on G. Le Bon's recent Paper on Dark Light.—G. H. Nievenglowski.—Already inserted.

Photography by Dark Light.—Gustave Le Bon.—Already inserted.

New Properties of the X Rays.—L. Benoist and D. Hurmuzesou.—Already inserted.

Experiments with Röntgen's Rays.—Albert Nodon.—Already inserted.

Permeability of Metals for the X Rays.—V. Chataud.—Already inserted.

The Photography of Metallic Objects through Opaque Substances by means of the Brush and the Induction Coil, without the Crookes Tube.—G. Moreau.—Already inserted.

Fluorides of Acids.—M. Meslans and F. Girardet.—The fluorides of acids are very easily obtained, and with yields nearly theoretical in quantity, by the action of the chlorides of acids upon zinc fluoride. These substances rapidly attack glass in presence of traces of water. In presence of this latter body they display a greater stability than the chlorides; they do not fume in the air; they react slowly with the alcohols to form ethers, and rapidly with ammonia to form the corresponding amides.

Preparation of the Fluorides of Acids.—Albert Colson.—The author has obtained and examined the fluorides of acetyl and propionyl.

On a Lithium Hydride.—M. Guntz.—This compound has the well-defined composition LiH. If heated in a current of nitrogen, the hydride is decomposed with the formation of a nitride. In a current of air it burns with the formation of lithia. The stability of lithium hydride at a red heat, its composition, its aspect, and its properties, quite distinct from the potassium and sodium hydrides, show a new distinction between the properties of lithium and those of the alkaline metals.

Journal für Praktische Chemie,
New Series, Vol. li., Parts 10 and 11.

Researches from the Chemical Institute of the University of Kiel.—These consist of the continuation of a memoir by C. Stoehr on the pyrazines and the piperazines. On comparing the three substances pyrazin, pyridin, and benzene, closely related in their constitution, it appears that with an increase of the molecular weight, the specific gravities increase and the boiling-points rise. On hydration, there does not occur successive change in the boiling-points, because the hexahydro-products of benzene and pyridin boil at a lower point than their fundamental substances, whilst with pyrazin the relation is inverse.

Researches from the Laboratory of the University of Freiburg, in Breisgau.—These researches comprise

a paper by Ad. Claus and Ann. Caroselli on orthoparadi-bromquinolin.

Conversion of Ketones into α -Diketones.—M. Filetti and G. Ponzio.—In a former paper the authors expressed a suspicion that the diketone is not formed by direct oxidation of the ketone. Subsequent experiments have shown that their conjecture is justified.

Derivatives of Metamethylorthouramidobenzoyl.—St. von Niementowski.—An account of carboxethyl-orthoamidoparatoluyamide, of nitrometamethylortho-uramidobenzoyl, of amidometamethylorthouramido-benzoyl, of dinitrometamethylorthouramidobenzoyl, of diamidometamethylorthouramidobenzoyl, and of the di-acetyl derivative of diamidometamethylorthouramido-benzoyl.

Analogy in the Behaviour of Halogen Alkyls with Sodium and analogous Metals on the one side and the Mercaptides on the other.—R. Otto and K. Mühle.—As far as the present experiments extend, all halogen-alkyls with fewer than 4 atoms of carbon yield alkylenes both with sodium mercaptides and with sodium.

Constitution of the η -Phenylpyrazolones.—R. von Rothenburg.—A controversial memoir against F. Stolz, L. Claisen, and E. Haase.

Diamidobenzoic Acids.—C. Haeussermann and H. Teichmann.—An account of the ethyl-ester of 3.5-di-amidobenzoic acid.

Constitution of Diazobenzene Compounds.—R. Walther.—It is clear that identical substances must be formed from diazobenzene and bromaniline on the one hand; and, on the other hand, from diazobrombenzene and aniline. It is manifest how, from one and the same diazobenzene, sometimes azo- and sometimes hydrazo-compounds are formed according to the ingredients to be combined.

MEETINGS FOR THE WEEK.

MONDAY, 2nd.—Society of Arts, 8. (Cantor Lectures). "Chemistry of certain Metals and their Compounds used in Building, and the Changes produced in them by Air, Moisture, and Noxious Gases, &c.," by Prof. J. M. Thomson, F.R.S.E.

— Medical, 8.30.

— Medical and Chirurgical, 8.30. (Anniversary).

— Society of Chemical Industry, 8. "Artificial Silk," by Messrs. Cross and Bevan.

TUESDAY, 3rd.—Royal Institution, 3. "The External Covering Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.

— Society of Arts, 8. "The Commercial Prospects of English East Africa, and British Central Africa," by G. Scott Elliott.

— Institute of Civil Engineers, 8.

— Pathological, 8.30.

WEDNESDAY, 4th.—Society of Arts, 8. "Röntgen's Photography of the Invisible," by A. A. Campbell Swinton.

— Society of Public Analysts, 8. "Estimation of the Diastatic Power of Malt," by Walter J. Sykes, M.D., and C. A. Mitchell, B.A. "Further Note on the Detection of Formalin," by H. Droop Richmond and L. K. Boseley. "The Detection of Formalin," by Otto Hehner. "Note on the Detection of Cotton-seed Oil in Lard," by E. J. Bevan.

THURSDAY, 5th.—Royal, 4.30.

— Royal Society Club, 6.30.

— Royal Institution, 3. "Masters of Modern Thought

— I. Voltaire," by The Rev. W. Barry, D.D.

— Chemical, 8. "On the Explosion of Cyanogen,"

by H. B. Dixon, E. H. Strange, and E. Graham.

— "On the Mode of Burning of Carbon," by H. B.

Dixon. "On the Detonation of Chlorine Pero-

oxide," by H. B. Dixon and J. A. Harker.

— "The Constitution of a New Acid resulting from

the Oxidation of Tartaric Acid," by H. J. H.

Fenton.

FRIDAY, 6th.—Royal Institution, 9. "The Tunnel under the Thames

at Blackwall," by A. R. Binnie, M.Inst.C.E.

— Geologists' Association, 8.

— Quekett Club, 8.

SATURDAY, 7th.—Royal Institution, 3. "Light," by Lord Ray-

leigh, F.R.S., &c.

— Medical, 7. (Annual Dinner).

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1893.

ON THE DEPRESSION OF EXPLOSIVE POTENTIALS, STATIC AND DYNAMIC, BY THE X RAYS.

By M. R. SWYNGEDAUW.

THE analogy between the ultra-violet rays and the Röntgen rays has led me to try the action of the latter upon the explosive potentials. Experiment has shown that the X rays lower explosive potentials according to the same general laws as the electrically active ultra-violet radiations.

The depression of the static explosive potentials is measured directly with the electrometer of Bichat and Blondlet, noting the explosive potential of the exciter, when illuminated by the rays or not illuminated.

The Crookes tube is traversed by the discharge of a Ruhmkorff coil actuated by two accumulators; it is placed parallel to the exciter, and at the distance of 25 c.m. from the latter. The exciter is formed of two iron spheres of 1 c.m. in diameter.

In an experiment where the explosive distance is 5½ metres, the exciter is discharged for a potential of 60 C.G.S. units, if *not* illuminated by the X rays. Under the influence of these rays the spark strikes at a potential of 58.8 C.G.S.

A black paper, a plate of glass or of wood, do not change, in an appreciable manner, the depression of the explosive potential.

A plate of brass, of the thickness of 0.5 m.m., completely suppresses the explosion.

The depression of the dynamic explosive potential is measured by the method of the two derived exciters formerly described (*Comptes Rendus*, Feb. 3, 1896). For the arc-lamp we substitute the Crookes tube; we place an opaque screen for the radiation (*e.g.*, a plate of brass), between the two derived exciters, $E_1 E_2$ and $N_1 N_2$.

Still in this form the method gives only negative results. This depends on the fact that the illumination with the Crookes tube is necessarily intermittent, and lasts only for a very small fraction of a second; a very fortunate coincidence is required, for the tube to be illuminated at the moment of the dynamic charge of the exciters.

To evade this difficulty I employ an artifice by means of which the Crookes tube is illuminated at the same time as the derived exciter is charged by the dynamic method (discharge of the condenser, GC_2).

In the secondary circuit of the Ruhmkorff coil we place a Crookes tube and a secondary exciter, S. This exciter is placed at the distance of 4 c.m., and opposite the poles of the principal exciter, $I_1 I_2$, which allows the charge of the condenser. The Crookes tube is placed opposite $E_1 E_2$, at the distance of about 25 c.m.

We actuate the Ruhmkorff coil; at each spark which strikes in S the coil discharges itself through the Crookes tube.

We charge the condenser slowly with a Holtz machine; when the potential of the exciter $I_1 I_2$ is close upon its static explosive potential, the one of its sparks which burst in S excites, by its ultra-violet radiations, the discharge of the exciter $I_1 I_2$ and of the condenser, and the derived exciters $E_1 E_2$ and $N_1 N_2$ are charged dynamically; $E_1 E_2$ are two rings of iron of 1 c.m. in diameter; $N_1 N_2$ are two rings of brass, also of 1 c.m. in diameter.

If $N_1 N_2 = 3$ m.m., the spark still bursts at $E_1 E_2$ when the explosive distance of $E_1 E_2$ is 5.40 m.m. under the influence of the X rays.

In the absence of these rays the poles of $E_1 E_2$ must be brought to the distance of 3 m.m., so that the spark may burst at $E_1 E_2$ rather than at $N_1 N_2$.

The interposition of a screen of paper or of glass does not diminish the depression in an appreciable manner. A plate of brass suppresses it entirely.

The spark of the same Ruhmkorff coil produces a lowering of the same order of magnitude if no screen is interposed between the exciter and the spark. A screen of wood, glass, or black paper arrests the active ultra-violet rays.

From these experiments we shall draw the following conclusions:—

I. When measuring the depression of the dynamic explosive potentials by the method of the derived exciters, we may detect with great distinctness the X rays.

II. The Röntgen rays lower the dynamic explosive potentials in much greater proportions than the static potentials.

—*Comptes Rendus*, cxxii., p. 374.

ELECTRICAL PHENOMENA PRODUCED BY THE RÖNTGEN RAYS.

By A. RIGHI.

IN the *Comptes Rendus* for February 3rd I find a communication, by MM. Benoist and Hurmuzescu, on the dissipation of electric charges obtained by the Röntgen rays. As I have executed similar researches at the same time as these physicists, and have communicated them to the Academy of Sciences of Bologna at its last Session, and as my results are not entirely identical with those of Benoist and Hurmuzescu, I solicit permission to give here a summary.

I have used a Mascart electrometer as a measuring apparatus. It is in connection with the substances upon which the X rays are caused to fall, and which emanate from a Crookes tube enclosed along with the apparatus yielding the discharges in a large metal case connected with the earth. The part of the case which is close to the tube is formed of a thick sheet of lead, having in the middle a round window of 1 c.m. in diameter, covered with a slender plate of aluminium, whence the rays issue.

I have found that a metallic disc communicating with the electrometer rapidly loses its charge, whether positive or negative. The duration of action necessary for the potential to fall from 7 to 3.5 volts is sensibly alike for a positive and for a negative potential.

With an initial positive charge the discharge is not complete; with a negative the substance is not merely discharged, but there is formed a positive charge.

If I cause the Röntgen rays to fall upon one of my photo-electric couples which are formed of a metallic tissue in connection with the earth, parallel and very near to a metallic disc in connection with the electrometer, I obtain deviation which is positive or negative, according to the nature of the metals of the couple, as with the ultra-violet rays.

A disc in its natural state is charged positively, if exposed to the new radiation (which takes place also on employing the ultra-violet rays). With this same disc the final positive potential is the same, whatever may be the initial value of the potential of the disc—positive, negative, or null. This final potential is higher for copper than for zinc, and still higher for retort-coke.

I find, besides, that a plate of glass, being nearly 1 c.m. in thickness, if placed on the path of the X rays, does not destroy their action, but enfeebls it appreciably. In the same manner the interposition of a thick plate of aluminium, or a thick board of deal, or even of the hand laid so as completely to cover the window, merely en-

feebleness more or less the action of the rays. I expect that similar results will have been obtained by other physicists.
—*Comptes Rendus*, cxxii., p. 376.

ACTION OF THE RÖNTGEN RAYS ON ELECTROSTATIC CHARGES, AND ON THE EXPLOSIVE DISTANCE.*

By J. J. BORGMAN and A. L. GERCHUN.

J. J. THOMSON has communicated to the readers of the *Electrician* (Feb. 7, 1896) an observation concerning the effect of the Röntgen rays upon electrostatic charges. According to him positive and negative charges are equally dissipated by the action of the rays. Our experiments do not completely confirm this fact.

A disc of zinc connected to an electroscope of medium sensitiveness and charged positively lost its charge almost instantly under the action of the Röntgen rays emanating from a Crookes tube at a short distance. For greater distances (1 metre) the dissipation of the charge still continues, but more slowly. After the loss of the positive charge, the leaves of the electroscope diverge anew, and indicate a negative charge, which goes on increasing up to a certain degree. If we communicate to the disc a negative charge the electroscope shows a much slower loss, which stops at a certain degree. The loss was smaller for low distances, and became moderately large if we removed the disc from the tube. When the stationary divergence of the electroscope was reached, the angle of divergence oscillated continually, becoming sometimes smaller, sometimes larger, according to the irregular progress of the interrupter. A leaf of aluminium (1 m.m. in thickness), connected with earth, weakened the action of the rays without altering their character. These experiments seem to show that the rays issuing from a Crookes tube may communicate a negative charge to the conductors.

In another experiment the rays fell upon two small platinum balls connected with a small Ruhmkorff apparatus. The distance of the balls was too great for a spark to overleap, yet the Röntgen rays falling upon the exciter produced immediately a lively projection of sparks. A thin leaf of aluminium connected with the earth, or plates of ebonite placed in the course of the rays, did not perceptibly modify the action. This experiment seems to prove that the Röntgen rays, like the ultra-violet rays, may increase the explosive distance of a static discharge.
—*Comptes Rendus*, cxxii., p. 375.

NATURE AND PROPERTIES OF DARK LIGHT.

By GUSTAVE LE BON.

BEFORE speaking of the new results of my researches I have the honour of informing the Academy that my experiments on the passage of ordinary light through opaque bodies have been repeated with full success by some observers, especially by Dr. Armeniac, of Bordeaux, and H. Murat, of Havre. The latter, following exactly my instructions, has succeeded in obtaining with the dark light results superior to those produced by the Röntgen rays.

The dark light and the rays of cathodic origin are certainly not similar radiations, for the dark light does not traverse substances such as ebonite, which are quite transparent to the Röntgen rays. M. Murat has sent me photographs of the inside of a fish, which I have the honour of presenting to the Academy. They show a sort

of successive dissection, layer by layer, such as I will explain in a future communication. The light of a simple lamp transformed into dark light by the procedure which I have indicated, that is to say, by its passage through the metallic plates, sufficed to obtain these results.

In my former papers I wished to publish only the crude results of my experiments. They seemed so inexplicable that it is necessary to indicate the theory which led me to execute them, and which permitted me to foresee them.

My purpose was to explore the region, still unknown, which separates the region of light from that of electricity. I supposed, as I said at the end of my first memoir, that the forms of energy should be infinite in number. We know merely a few, such as heat, light, and electricity. But these known forms should be connected together by intermediate forms; these latter are still unknown, because we do not possess instruments capable of translating them in a manner perceptible to our senses.

In order to discover one of these modes of intermediate energy, we must first find an instrument capable of showing vibrations less numerous than those of light and more numerous than those of electricity. Photographic plates being under certain conditions still sensitive to the vibrations relatively few in number situate beyond the visible spectrum, it was to be hoped that they might be sensitive to vibrations much more numerous. If it were really thus we should find ourselves exactly in the zone intermediate between light and electricity. But then this new form of energy ought to possess some properties intermediate between light and electricity. It would perhaps not propagate itself like light, and perhaps might propagate itself like electricity. In this latter case the vibrations should not be arrested by opaque metallic bodies, whatever their thickness. To verify these conceptions I devoted researches pursued during two years, and I wished to expound in my first paper merely the most incontestible results. Without the theory which guided us we should have been arrested by the failures which attended our first researches.

The demonstration of the passage of light through thick plates of metal was effected very rapidly, but the results were attended with partial failures, which embarrassed me for a long time. Most frequently the image was perfect at the external margins of the plate, or at its centre, and then suddenly stopped. On employing two metals we either promoted or hindered the experiment. It is thus, for instance, that the presence of a sheet of polished tin behind the sensitive plate decidedly hinders the passage of the light through the plate of aluminium covering the proof. Sometimes very satisfactory results were obtained on placing the glass before or behind the proof. Sometimes the image was negative and sometimes positive. Evidently electric influence must intervene, but no less evidently the effects produced were due to the action of light, since, all the conditions of the experiments being alike, the images were obtained only when the light fell upon the opaque plates covering the frame. In a future note I will explain how, by means of an instrument infinitely sensitive (a galvanometer with a frame movable, in an intense magnetic field produced by an auxiliary current of 30 volts and 2 ampères), I hope to demonstrate the liberation of electricity during the formation of ordinary photographic images. At present I wish to explain merely the experiments concerning the passage of light through opaque bodies and the transformations which it then undergoes.

In the experiments which are to follow each proof receives two sensitive plates, one on its upper part and one on its lower part: one of them serves as a check,—that is, it shows by a previous sojourn of the fitted frame in darkness, that the image produced on the plate covering the second part of the proof is produced only under the influence of the dark light. In this manner we totally eliminate all hypotheses which might be formed on the causes of the formation of the image,—light stored up, pressure, heat, electricity, &c. Only the light which has

* Compare with paper by R. Swyngedauw (see p. 109).

traversed the plate, and has been transformed into dark rays, produces the image, since without such light the image is never produced.

Now follow a series of experiments which would seem very contradictory if we had not, for their explanation, the theory which I have propounded, and if we consider that the dark light must, like ordinary light, always propagate itself in a right line.

The frame being covered with one of the metals which I have indicated—for instance, iron or aluminium—one-half of the metal plate is covered with about ten leaves of paper superimposed, which will suffice, with the exposure which we employ, to arrest the formation of the image on a sensitive plate exposed beneath a proof. Now on developing we find that the image is absolutely equal in intensity both under the part covered merely by the metal and in the part where the metal itself is covered with ten thicknesses of paper. If upon this same metal plate we superimpose larger discs of iron, of several centimetres in thickness, we still find that these discs, notwithstanding their thickness, leave no trace upon the image.

These experiments, which have been repeated and modified in every way, are fundamental. They show us at first that the degree of thickness of the opaque plates is without importance for the passage of light, just as it would be for the passage of electricity. The experiments show us that dark light in its propagation follows other laws than those of ordinary light. In fact, if dark light were propagated in a right line, the parts of the proof protected by the discs and the leaves of paper placed upon the metal plates would be indicated by a shadow on the glass. But if the dark light obeys the laws of propagation of electric waves, if one point of the metal receives the rays they are propagated over the entire surface.

We may thus transform light into radiations which are propagated like electric currents. Still they are not electric radiations, since ordinary electric currents do not produce the same effect.

We find ourselves thus in presence of a mode of energy which is no longer light, since it has only a part of its properties and does not obey its laws of propagation. Neither is it electricity, since electricity in its known form does not produce the same effects. Dark light must probably be considered as a new force in addition to the small number already known.—*Comptes Rendus*, cxxii., p. 386.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JANUARY 31ST, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, February 10th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Jan. 1st to Jan. 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined one was recorded as "clear but dull," the remainder being clear, bright, and well filtered.

The rainfall at Oxford during the month has been 0.63 inch, as against 2.16 inches, the average for the past 29 years; this shows a deficiency of 1.53 inches, as compared with the average.

The exceptionally small rainfall in the Thames Valley during January has improved the condition of the river and made filtration operations remarkably effective.

The quality of the supply during the past month, regarded both from the chemical and bacteriological point of view, has been exceptionally good.

Our bacteriological examinations for the month of January give the following numbers of colonies per cubic centimetre:—

	Colonies per c.c.
Thames water, unfiltered	1824
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	50
Ditto ditto lowest	24
Ditto ditto .. (12 samples) mean	36
New River water, unfiltered	1525
New River water, from the Company's clear water well	31
River Lea water, unfiltered	2005
River Lea water from the East London Com- pany's clear water well	24

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

THE WALRAND-LEGÉNEL PROCESS FOR STEEL CASTINGS.

By SERGIUS KERN, M.E. St. Petersburg.

IN 1894, Mr. George Snelus, F.R.S., read a paper under this heading at the May meeting of the Iron and Steel Institute in London. The paper gave an elaborate statement of the working of small Bessemer converters, at Paris and Hagen, by the Walrand-Légénél method.

At the Franco-Russian Works, St. Petersburg, this process was lately started, with good success, by the inventors. We witnessed five operations, consecutively made, in one afternoon. The converter is for a charge of 300 kilos., which is run from a Walrand cupola, working very regularly, and consists of Ayresome pig-iron, scrap (runners, top-ends, &c.), and a small quantity of ferro-silicium, in order to have in all 3 to 3.15 per cent of silicon in the metal to be converted into steel.

At a certain time during the third period of the Bessemer process a charge of ferro-silicium was added, an afterblow made, and, finally, silicospiegel added.

The resulting steel is poured into ladles, into which about 0.1 per cent of metallic aluminium is thrown.

The steel is hot and readily fills the mouldings. The metal in the castings is soft and ductile. In order to give an idea of the *modus operandi*, we took the following notes:—

First blow, commenced at 1.51 p.m.; metal from fourth blow poured into moulds at 4.5 p.m. So that in two hours fourteen minutes four blows were made.

Description of the first blow, which was the coldest of all, being the commencement of operations:—

1. Pig-iron poured into the converter, and blow commenced at 1.51 p.m. (pressure of air about 32 lbs.).

2. Commencement of the second period, line D of sodium well marked, 2.2 p.m. (pressure of air about 15 lbs.).
3. Converter turned, to add ferro-silicium, and commencement of afterblow at 2.8½ p.m. (pressure of air, 22 to 24 lbs.).
4. Silicospiegel added at 2.10½ p.m.
5. Commencement of the pouring of steel into ladles, 2.14 p.m.

The same process, but with two (nearly one ton each) converters, has been started also at the Baltic Ship-building Works, St. Petersburg, and with encouraging success.

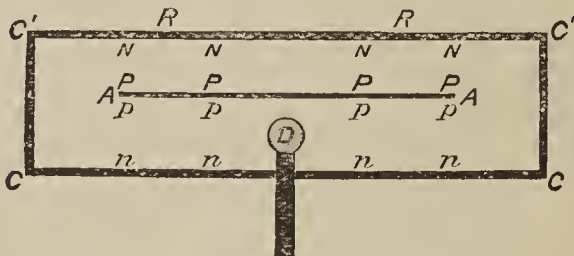
We remarked only that for small castings up to 100 to 150 kilos. crucible steel is more useful, being a little colder, with less gases in solution, and therefore more quiet. It better fills the small mouldings attached to a general runner.

Having seen the practice of the new process, we find it specially adapted to large and medium sized castings. Sometimes, as a result of working, very small castings are shown in order to popularise new processes, but one must believe that in such a case the small castings are picked out of series of similar articles, bad ones being rejected.

ON THE GENERATION OF LONGITUDINAL WAVES IN ETHER.*

By Lord KELVIN, F.R.S.

In a short note recently published in *Nature*, of which a copy is appended, I suggested an arrangement of four insulated and electrified spherical conductors with their centres in one line, giving rise to ethereal waves in the surrounding atmosphere, of which the disturbance in the line of centres is essentially longitudinal. But at any finite distance from this line there must also be laminar or distortional waves of the kind expressed in Maxwell's equations. The object of my present communication is to show an arrangement by which a large space of air is traversed by pressural disturbance, or by waves essentially longitudinal, or by condensational-rarefactional vibrations; with but a very small proportion, practically evanescent, of laminar waves.



Let AA be a plane circular metal plate insulated within a metal case, CC'C', as indicated in the drawing. Let D be a discharger which can be pushed in so as to make contact with A.

Let A be charged to begin with, positively for instance as indicated by the letters P P p p; N N n n showing negative electricity induced by it. Let now the discharger be pushed in till a spark passes. The result, as regards the space between AA and the roof RR over it, will be either an instantaneous transmission of commencement of annulment of electrostatic force, or a set of electric waves of almost purely longitudinal displacement, according as ether is incompressible or compressible.

Hence, if the theory of longitudinal waves, suggested by Röntgen as the explanation of his discovery (for the consideration of which he has given strong reasons), be true, it would seem probable that a sensitive photographic

plate in the space between AA and RR should be acted on, as sensitive plates are, by Röntgen rays. Either a Wimschurst electrical machine or an induction-coil, adapted to keep incessantly charging AA with great rapidity, so as to cause an exceedingly rapid succession of sparks between D and A, might give a practical result. In trying for it, the light of the sparks at D must be carefully screened to prevent general illumination of the interior of the case and ordinary photographic action on the sensitive plate.

The arrangement may be varied by making the roof of sheet aluminium, perhaps about a millimetre thick, and placing the sensitive photographic plate, or phosphorescent substance, on the outside of this roof, or in any convenient position above it. When a photographic plate is used there must, of course, be an outer cover of metal or of wood, to shut out all ordinary light from above. This arrangement will allow the spark gap at D to be made wider and wider, until in preference the sparks pass between AA and the aluminium roof above it. The transparency of the aluminium for Röntgen light will allow the photographic plate to be marked, if enough of this kind of light is produced in the space between the roof and AA, whether with or without sparks.

The new photography has hitherto, so far as generally known, been performed only by light obtained from electric action in vacuum; but that vacuum is not essential for the generation of the Röntgen light seems demonstrated by an experiment by Lord Blythwood, which he described at a meeting of the Glasgow Philosophical Society on February 5th. As a result he exhibited a glass photographic dry plate with splendidly clear marking which had been produced on it when placed inside its dark slide, wrapped round many times in black velvet cloth, and held in front of the space between the main electrodes of his powerful Wimschurst electrical machine, but not in the direct line of the discharge. He also exhibited photographic results obtained from the same arrangement, with only the difference that the dark slide, wrapped in black velvet, was held in the direct line of the discharge. In this case the photographic result was due, perhaps wholly, and certainly in part, to electric sparks or brushes inside the enclosing box, which was, as usual, made of mahogany, with metal hinges and interior metal mountings. I have suggested to him to repeat his experiments with a thoroughly well-closed aluminium box, instead of the ordinary photographic dark slide which he used, and without any black cloth wrapped round outside. The complete metallic enclosure will be a perfect guarantee against any sparks or brushes inside.

If the arrangement which I now suggest, with no sparks or brushes between AA and the roof, gives a satisfactory photographic result, or if it shows a visible glow on phosphorescent material placed anywhere in the space between AA and the roof above it, or above the aluminium roof, it would prove the truth of Röntgen's hypothesis. But failure to obtain any such results would not disprove this hypothesis. The electric action, even with the place of the spark so close to the field of the action sought for as it is at D, in the suggested arrangement, may not be sudden enough or violent enough to produce enough of longitudinal waves, or of condensational-rarefactional vibrations, to act sensibly on a photographic plate, or to produce a visible glow on a phosphorescent substance.

Extract from *Nature*, referred to above:—

"Velocity of Propagation of Electrostatic Force.

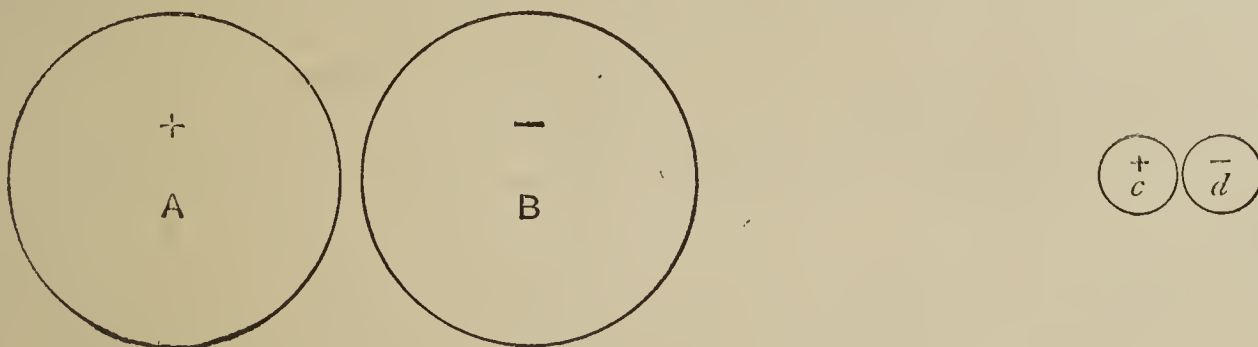
"Dr. Bottomley's note published in *Nature*, of Jan. 23, quotes an extract from my Baltimore Lectures of October, 1884, in which this subject is spoken of, with an illustration consisting of two metal spheres at a great distance asunder, having periodically varying opposite electrifications maintained in them by a wire connecting them through an alternate current dynamo.

"For an illustration absolutely freed from connecting

* A Paper read before the Royal Society, February 13, 1896.

wire and all complications, consider four metal spheres, A, B, *c*, *d*, with their centres all in one straight line; their relative magnitudes and positions being such as shown in the accompanying diagram. Let each of the four be initially electrified, A and *c* positively, B and *d* negatively. Let the charges on *c* and *d* be so strong that a spark is only just prevented from passing between them by the influence of B and A. Let A be gradually brought nearer to B till a spark passes between them. Will the consequent spark between *c* and *d* take place at the same instant or a little later? It is not easy to see how this question could be answered experimentally; but remembering the wonderful ingenuity shown by Hertz in finding how to answer questions related to it, we need not, perhaps, despair to see it also answered by experiment.

"The elastic solid theory restricted to the supposition of incompressibility (which is expressed by Maxwell's formulas) makes the difference of times between the two sparks infinitely small. The unrestricted elastic solid theory gives for the difference of times the amount calculated according to the velocity of the condensational-rarefactional wave.



"But I feel that it is an abuse of words to speak of the 'elastic solid theory of electricity and magnetism,' when no one hitherto has shown how to find in an elastic solid anything analogous to the attraction between rubbed sealing-wax and a little fragment of paper; or between a loadstone or steel magnet and a piece of iron; or between two wires conveying electric currents. Elastic solid, however, we must have, or a definite mechanical analogue of it, for the undulatory theory of light and of magnetic waves and of electric waves. And consideration of the definite knowledge we have of the properties of a real elastic solid, which we have learned from observation and experiment, aided by mathematics, is exceedingly valuable in suggesting and guiding ideas towards a general theory which shall include light (old and new) old and new knowledge of electricity, and the whole of electromagnetism.—KELVIN."

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 90.)

On the Flame Spectrum of Chloride of Calcium.—I checked the spectrum of pure oxide by reducing it to chloride. In the previous chapter I described the method by which I obtained the chloride of calcium used in the first experiment.

After having heated to redness, long enough to drive off sodium brought by the air, a thin concave sheet of platinum containing a cone of spongy iridium, I poured over the cone enough fused chloride of calcium to thoroughly soak it. I then projected on to the top of the cone the point of an oxyhydrogen blowpipe, in which spectrum analysis only showed very transient traces of the sodium D line. At the very moment of contact I

saw the sodium line of remarkable strength, but it became weaker until there was nothing but a trace seen in the blowpipe flame in air: this happened when the chloride was so far dissociated that it had become an oxychloride, infusible at the fusing-point of platinum.

When, instead of heating the chloride of calcium in an oxyhydrogen blowpipe on a cone of spongy iridium, it is fused on to an iridio-platinum loop overlaid with sodium, or on to a hook of iridium alloyed with 20 per cent of platinum, or on to a small cone of pure carbon ending in a point, and if the loop, hook, or needle-point thus coated were introduced into the envelope of an oxyhydrogen or oxy-coal-gas blowpipe, spectrum analysis shows the sodium line at once, *strongly at first*, but gradually getting fainter until it is no stronger than it is seen in a blowpipe without the chloride.

The spectrum of *oxide* of calcium exhibits a remarkable constancy of position. From the moment of its appearance in an oxyhydrogen or oxy-coal-gas blowpipe, until the highest temperature attainable by burning hydrogen in oxygen is reached, no matter whether there be more or fewer bands and hazy lines, or whether the back-

ground be dark or shows a continuous luminous spectrum, the position of the bands and lines is absolutely the same. The flame spectrum of *chloride* of calcium acts quite differently. Up to the moment of greatest luminosity, which appears to coincide with the spectrum of the chloride itself, the bands, although distinct, are very hazy, possibly owing to the width of the slit; they appear to me to be in a permanent state of slight undulation until the chloride is completely reduced to oxychloride or oxide of calcium, or at least until the gases and vapours in the air cease to smell of chloride of calcium and hydrochloric acid and begin to smell of oxide of calcium.

On account of the dissociation of chloride of calcium in an oxyhydrogen or oxy-coal-gas flame, I consider the use of the blowpipe much less suitable with chloride than with oxide, and especially with *granular* oxide, for observing the lines characteristic of the flame spectrum of calcium, much less for measuring the position of these lines.

I frequently noticed that, at the instant of introducing chloride of calcium into the hottest part of the blowpipe, the compound became *incandescent*, and emitted *white* light; this afterwards became *bluish* white. The calcium colour only appeared in the blowpipe at a considerable distance from the point of introduction. This phenomenon is not seen when using oxide or sulphate of calcium instead of chloride of calcium, on an iridio-platinum loop overlaid with pure iridium. When using oxide made by calcining nitrate of calcium, the flame was deep brownish red or chocolate colour, from the instant the compound was volatilised in any part of the flame. It appears, then, that the emission of the bluish white light coincides with the dissociation of the chloride.

In order to ascertain exactly the cause of the appearance of the sodium line with the chloride, I repeated the experiments, using, instead of the blowpipe, a spark and discharge from an induction-coil *without* and with a condenser. I thus found that the colour of the spark varied with the amount of chloride of calcium used, and that

the sodium line was a little fainter than when using the blowpipe.

This line persisted with the same relative intensity throughout the experiments, and was *stronger* than that seen at the same time in the surrounding air, when substituting *uncovered* balls of pure platinum for those covered with fused chloride of calcium, whether *anhydrous* or *moistened* with a saturated solution of the compound.

It undoubtedly follows from these observations that, during the conversion of oxide into chloride of calcium, and, I may add, throughout the experiment in air containing sodium, the compound occludes sodium in spite of my extreme care. I must add, to be accurate, that during these researches the state of the air was not all that could be wished for. The hygroscopic quality of chloride of calcium doubtless aided in attracting the sodium. I proved that, on evaporating water, condensed from the air in which I was working, collected on the outer surface of a platinum dish containing ice, the residue left contained an appreciable amount of sodium. Besides, the facts I have yet to describe will prove that the presence of sodium is *solely* due to this cause.

I have submitted to spectrum analysis a spark flashing from the surface of a hydrochloric solution of chloride of calcium, made from elements free from sodium, in the tube which held it, in pure air.

With this object I distilled with the greatest care, on the one hand, a 10 per cent solution of hydrochloric acid in a platinum apparatus filled with purified air. After distilling it, I closed the receiver by a platinum plug fitted to the tube.

Spectrum analysis of a Bunsen flame, into which I gradually introduced by means of a platinum tube about 1 c.c. of the condensed acid, *did not show the sodium line.*

On the other hand, I made some pure oxide of calcium, by projecting into some carbonate of calcium, on a recently heated sheet of platinum, a coal-gas and air blowpipe flame, until spectrum analysis of the calcium flame ceased to show the sodium line. The accidental traces of sodium being completely eliminated, I at once put the sheet of platinum with the oxide under a small glass bell-jar full of purified air, with its rim ground and greased, standing on a sheet of smooth and polished glass, and I took the whole into the large room devoted to spectroscopic work.

Having heated to whiteness a small platinum dish containing a hollow cone, the top of which was about 2 m.m. below the edge of the dish, I poured over it a suitable quantity of oxide of calcium, and I put the dish with the oxide on the three-pronged support of the small apparatus* intended to saturate an electric spark or discharge with a saline solution. I quickly lowered the dish to the bottom of the little apparatus filled with purified air. Whilst a current of purified air was passing through the apparatus I poured into it, by means of a small recently-heated platinum funnel, enough distilled hydrochloric acid to convert the oxide of calcium into chloride, to make the solution decidedly acid, and to raise the liquid to the top of the hollow cone. I then put into the top of the apparatus the pure rubber plug, fitted with its pointed platinum rod which had been washed and heated to redness at the same time as the funnel.

Having caused air, which had been purified and saturated with moisture, to circulate in the apparatus, I stopped the current by closing the taps in the tube. By using the direct-vision spectroscope by M. Hilger, and the Steinheil spectroscope, I analysed an induction spark without a condenser, flashing from the top of the platinum cone covered with the calcium solution; towards the point of the platinum rod, which was from 2 to 4 m.m. long, I noticed that the *sodium D line was entirely absent* from the spectrum. This consisted entirely of either the electric spectrum of calcium, or of this spectrum together with Fraunhofer's hydrogen C line, or, simultaneously,

the electric spectrum of calcium, the red hydrogen line and some air lines, according to the length of the spark and the intensity of the electric discharge.

Having replaced the air in the apparatus by pure hydrogen, I found that the sodium line was still absent from the spectrum. Besides the electric spectrum of calcium, M. Rommelaere and I always saw the red hydrogen line, but we tried in vain to see Fraunhofer's F, G, and H hydrogen lines.

Having found, by spectroscopic observations, that the air of the large room I was working in was comparatively pure, I withdrew from the above-mentioned apparatus the small platinum dish with the liquid calcium salt, and immediately put some of the liquid into pure hydrogen burning in air, by means of a recently heated platinum spiral. Spectrum analysis of the blowpipe, thus charged with calcium, showed the *flame spectrum* of chloride of calcium, *entirely* free from the sodium line. I repeated the experiment several times, and always with the same result.

I carried a small water-bath, heated by a Bunsen burner, into the large room devoted to spectroscopic work, and I put on this bath the small platinum dish containing the hydrochloric solution of chloride of calcium. Whilst it was being evaporated, I analysed the calcium liquid, at intervals of ten minutes, by introducing portions of it into a burning hydrogen blowpipe by means of a platinum spiral. As the air of the room was being more and more charged with sodium, owing to the presence of several people for more than an hour, I judged it necessary to provide a means of comparison during the analysis. For this purpose I arranged a second hydrogen blowpipe as near as possible to the prism, in such a way that the spectra of the two flames were as accurately as possible superposed. By doing this, I found that the solution became more and more charged with sodium as it evaporated; and long before it was so concentrated as to solidify on the spiral when cold, the sodium line was seen to be brighter than that in chloride of calcium made and fused in contact with the surrounding air.

I tried to verify the above results by substituting an acid solution of nitrate for the hydrochloric solution of chloride of calcium. For this purpose, I made this solution of oxide of calcium free from sodium, and a 10 per cent solution of nitric acid, distilled, collected, and kept in platinum, working in exactly the same manner as I did when making the hydrochloric solution of the chloride. I thus found that the acid solution of nitrate of calcium, when put into a spark or flame, showed, on spectrum analysis, a spectrum quite free from the yellow sodium line, and that the solution, when evaporated on a bath in the surrounding air, collected sodium from the air in the same way as the hydrochloric solution of chloride of calcium.

Thus it is proved, beyond a doubt, that the presence of sodium in the flame and electric spectra of chloride and nitrate of calcium, made from pure elements, but in contact with the surrounding air, is due to the occlusion of sodium present in the air.

(To be continued).

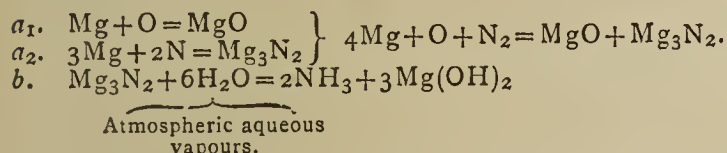
The British Adulteration Laws.—(*Chem, Zeitung*).—The annual report of Dr. Sedgwick Saunders, the Public Analyst for the City of London, discusses the position of British analysts under the "Food and Drugs Adulteration Act." The hopes of an alteration and an improvement in legislation are still unfulfilled. The official chemists of Somerset House are still empowered to criticise and reject any analysis, even if it has been obtained from the most eminent analysts, and the decisions of many Courts throughout the country are still in flat defiance not merely to Science, but to practical common sense. The report of the Special Parliamentary Committee on this subject, in spite of its bulk, leaves much to be desired as regards the thoroughness of investigation,

* See CHEMICAL NEWS, vol. lxxii., p. 248.

COMBINATION OF ATMOSPHERIC AND CHEMICAL NITROGEN WITH METALS.

By P. L. ASLANOGLU.

PERHAPS it will be remembered that I published an article in the CHEMICAL NEWS of August 29, 1890 (vol. lxii., p. 99), entitled "Ammonia formed by Burning Metallic Magnesium in Contact with Atmospheric Air," and in which I pointed out the possibility of the estimation of the composition of the atmosphere by these means. In it I gave approximately the formulæ of the reactions, viz.,—



In communicating to the CHEMICAL NEWS the above fact, I did not state then any quantitative results; it was merely published as a notice. By further experiments in the same year, I found that the ammonia formed during the combustion of metallic magnesium in the open air was the following:—

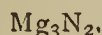
The resulting substance was of a dirty grey greenish yellowish colour (a colour rather difficult to define), smelling strongly of ammonia. When acted upon by water it rose in temperature considerably, and if handled with slightly moist hands it felt hot and irritating to the skin.

100 grms. of this substance, $2\text{NH}_3 + 3\text{Mg}(\text{OH})_2$, gave 15.438 grms. of ammonia, equal to 12.7 nitrogen, which if calculated on Mg_3N_2 minus the six atoms of water (atmospheric aqueous vapour), will give 26.416 nitrogen as percentage, the molecular weight of Mg_3N_2 being 100; therefore, by my method, I found that 26.416 per cent of nitrogen is taken from the atmosphere, the theoretical amount of nitrogen in Mg_3N_2 being 28 per cent as against 26.416 per cent found by my experiments.

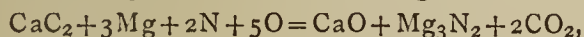
	Per cent.
Theory	28
Found	26.416

Difference (in deficiency) 1.584

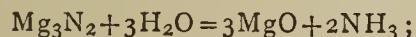
This reaction leads to the formula—



In an article entitled "Direct Combination of the Nitrogen of the Atmosphere with Metals in the State of Magnesium, Aluminium, Iron, Copper, &c., Nitrides," by A. Rossel, which appeared in the CHEMICAL NEWS (vol. lxxiii., p. 62), the author seems to have obtained a nitride of magnesium by heating the metal with calcium carbide, and to have found that 23 per cent of nitrogen is taken from the atmosphere, his formula being,—



and when acted upon by water ammonia was given off according to his formula,—



he found 23 per cent N, as against 28 per cent demanded by theory.

	Per cent.
Theory	28
A. Rossel's experiments	23

Difference (in deficiency) 5

Which is further removed from the theory than what I found by 3.416 per cent.

But, as you will see by my above formula (a_1), the magnesium first burnt with the oxygen resulted in magnesium oxide, and then an additional magnesium burnt,

so to speak, with the nitrogen formed magnesium nitride, as per formula a_2 ; but the presence of atmospheric aqueous vapours acting at the same time on the magnesium nitride formed ammonia and magnesium hydrate, as per formula b . Thus, the resulting substance of my experiments was nothing more than a mixture of ammonia and magnesium hydrate.

But what becomes of the aqueous vapours of the atmosphere in the experiments of A. Rossel?

I have obtained magnesium nitride in a yellow form by the following method, giving 26.82 per cent of nitrogen, and corresponding to the formula Mg_3N_2 , and higher than that of A. Rossel's experiments.

	Per cent.
Obtained	26.82
A. Rossel's experiments	23
Difference less from my expts.	3.82

I must mention here that Professor W. Ramsay's magnesium nitride in his work with argon finds 26.1 per cent nitrogen taken from the atmosphere (*vide* CHEMICAL NEWS, vol. lxxi., p. 52). Therefore the percentage of nitrogen taken from the atmosphere in the form of magnesium nitride is:—

Identical methods.		
Calcium carbide method.		
Prof. W. Ramsay's, 1894.	A. Rossel's, 1896.	P. L. Aslanoglou's, 1890.
Per cent.	Per cent.	Per cent.
26.1	23	1st meth., 26.416
		2nd meth., 26.82
		Chemical nitrogen.
		3rd meth., 27.213
	Theory, 28	
	Difference (in	
	1.9 deficiency), 5	(1) 1.584
		(2) 1.18
		Chemical nitrogen.
		(3) 0.787

Second Method.—A quantity of metallic magnesium powder was well dried at 100° C. for several hours, and air was slowly bubbled through a series of tubes:—

1. Three tubes concentrated sulphuric acid;
2. Three tubes caustic potash;
3. Three tubes alkaline pyrogallate;
4. Three tubes fused calcium chloride;
5. Three tubes soda-lime;

and condensed into a long combustion tube containing the dried metallic magnesium in powder. After time had been allowed to expel all air from the whole apparatus, the magnesium was heated, and any gases unacted upon were cooled by a direct condenser (Graham's) and received in a vacuum tube with magnesium electrodes. When the action was finished, the vacuum tube was sparked through, and I distinguished the nitrogen spectrum, but some time after the nitrogen acted on the magnesium electrodes, attacking at the same time the glass and leaving a fine yellowish film on the sides of the tube; eventually the nitrogen spectrum disappeared, giving only a bluish fluorescence.

Third Method.—By ammonia gas, otherwise chemical nitrogen. The plan adopted was similar to the second method, except the absorption tubes, which were in series of six tubes caustic potash and six tubes lime.

The vacuum tube was sparked through when I distinguished the hydrogen spectrum. This sample of magnesium nitride was of a lighter colour than that found in the second method, and gave 27.213 per cent nitrogen, as against theory 28 per cent.

	Per cent.
Theory	28
Found	27.213
Difference (in deficiency)	0.787

I have tried metallic copper, iron, zinc, aluminium, and clay in fine powder, strongly heating them in the open air, but I failed with the first three; while aluminium gave a somewhat similar reaction to magnesium, but not distinctly enough to encourage me to pursue my researches by this method, or it may be due to the temperature not being high enough. Clay, when strongly heated, gave an ammonia smell which soon disappeared. I have often noticed, in smoking tobacco in a clay or meerschaum pipe, an ammoniacal smell. Is this due to results as above, or to the N_2 of nicotine, $(C_5H_7)_2N_2$? And when a fairly old clay or meerschaum pipe is heated by a Bunsen burner there occurs a most violent explosion, shattering it into atoms. I have followed up my investigations on atmospheric and chemical nitrogen since 1890 in the form of nitrides, and I must say that nitrogen is a difficult agent to work with, and here is another instance which was published by me in the *CHEMICAL NEWS*, vol. lxiv., p. 313, "The Supposed Copper Nitride." In the *Phil. Mag.*, 3, xix., 100, July-Dec., 1841, Mr. W. R. Grove, M.A., F.R.S., refers to some electrolytical experiments in which, when a piece of metallic copper is connected with the positive pole and the negative pole of a battery with a platinum plate in a solution of ammonium chloride, copper nitride was formed. But on repeating his experiment several times I found that no copper nitride is formed, but only a mixture of copper oxide with metallic copper, corresponding to the formula $Cu_2O + Cu$. And in the same volume of the *Phil. Mag.* (p. 102) Mr. W. R. Grove says it may be worth remarking that the quantities of nitrogen which enter into combination with the metals are in proportion to their affinity for oxygen, and it may perhaps be considered an argument in addition to the many already advanced to prove that nitrogen is an oxide.

A. Rossel gives us only the percentage of nitrogen taken from the atmosphere in the case of magnesium, although he has obtained nitrides of aluminium, iron, copper, &c. It would be interesting to know the percentage of nitrogen which enters into combination with these metals.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, February 28th, 1896.

Prof. JOHN PERRY, Vice-President, in the Chair.

SIR D. SALOMONS showed some Experiments with Incandescent Lamps.

A large electro-magnet is excited by means of a continuous current, while an alternating current is passed through an incandescent lamp. On bringing the lamp near the magnet the filament is set in vibration, which, if the lamp is brought sufficiently near the magnet, is sufficiently intense to break the filament. The number and position of the nodes formed in the vibrating filament are found to be independent of the natural period of the filament, but depend on the frequency of the alternating current.

Prof. S. P. THOMPSON asked whether it was not found that the number of segments into which the filament is divided depend to some extent on the natural period of the filament.

Prof. AYRTON said that the magnetic leakage was very large with the arrangement adopted, and he would like to know whether this method was a more sensitive one for mapping out the field than those ordinarily employed. In an instrument designed by Prof. Perry and himself, an alternating current was passed through a wire stretched between the poles of a magnet, and the tension of the wire was altered till the vibrations set up were a maxi-

mum. The natural period of the wire, and hence the frequency of the alternating current, was then deduced from the tension, &c. In Prof. Ewing's magnetic curve tracer, on the other hand, the natural period of the stretched wire was made as different as possible from the period of the alternations which were to be observed, so that the natural vibrations of the wire did not influence the result. The author's arrangement appeared to him (Prof. Ayrton) to be intermediate between these two, and it would seem that the natural period of the filament would, to a certain extent, influence these results.

Prof. PERRY suggested that the lamp might be held in a very steady support, so that after the large vibrations due to the natural period of the filament had died out, the vibrations of the period of the alternations alone could be observed.

Sir D. SALOMONS, in his reply, said that the arrangement was not intended for making measurements. A lamp had been fixed in a steady clamp and the current passed for many hours, but the character of the vibrations remained unaltered. He had found the vibrating filament useful for microscopic work where any surface rather than a line of light was required.

Prof. FLEMING read a paper, by himself and Mr. PETAVEL, on "*An Analytical Study of the Alternating Current Arc.*"

The first part of the paper consists of an analytical study of the distribution of light throughout the various radiating regions in the arc when supplied with electric power of known constant amount, the periodic variations of the current through the arc, and of the potential difference between the carbons being at the same time recorded. The power was measured by means of a bifilar wattmeter; while, by means of a series of mirrors and a rotating disc carried by a synchronising alternating current motor, the mean value of the light taken from any part of the arc was compared with the instantaneous value of the light taken from the same part of the arc, and taken at any assigned instant during the period. Thus, the arc itself was its own standard, and difficulties due to slow variations in the mean light of the arc disappear.

The facts observed may be summed up as follows:—The purple light of the true arc undergoes a periodic variation, and, as far as the eye can judge, is completely extinguished during a certain interval during the phase; it has equal maxima values during the period, at instants slightly lagging behind the instants of maximum power expenditure in the arc. On the other hand, the illuminating power of the carbon crater varies between a minimum value and two unequal maxima; the greater maximum occurring when the carbon is positive and at an instant slightly lagging behind the instant of maximum power expenditure in the arc. The second part of the paper consists of a comparison of the efficiency of the alternate current arc regarded as a light-giving agent, as compared with that of a continuous current arc, taking the same mean power. Using two arcs which may be regarded as typical of those used in practice, the mean spherical candle-power was compared for equal expenditure of power in the arcs; and it was found that, for the alternating current arc employed, the total mean spherical candle-power was always less than that of the continuous current arc. Lowering the frequency seems to decrease the efficiency of the alternating current arc.

Prof. AYRTON said the behaviour of the alternate current arc was of great interest, for the power supplied could not be measured by simply multiplying the current by the electromotive force, since the current lags behind the volts. The resistance, *i.e.*, the ratio of the current to the E.M.F., also lags, but the authors do not appear to have made any attempt to measure the *true* resistance. The authors were to be congratulated on the guarded tone they had adopted as to the bearing of these experiments on the question of the relative efficiency of the alternating and continuous current arcs. In a previous communica-

tion, one of the authors had stated that the alternating current arc must necessarily be a less efficient light-producing agent than the continuous current arc. Although the last set of curves given in the paper might appear to support this supposition, he (Prof. Ayrton) felt that the difference obtained was probably due to the fact that the alternating current arc was not being worked under proper conditions. The quality of the carbons and the length of the arc have a most important influence on the efficiency of an arc. At present, our knowledge is not sufficient to allow of our stating definitely whether or not an alternating current arc can be made as efficient as a direct current arc, but there is no doubt that it will be possible to get much better results than are at present attainable.

Prof. S. P. THOMPSON said that when the fact of the existence of the difference in phase between the current and volts in an alternating arc was first published, he made some experiments which showed that there was a lag, and not a lead, *i.e.*, that the arc acted as if it possessed self-induction. The resistance also lagged, and he thought this lag might be due to a thermal lag. The temperature of the arc will lag behind current, both when it is increasing and when it is decreasing, and if the resistance of the arc depends on the temperature of the vapour in the arc, then the resistance would also lag behind the current. It was not possible from *à priori* reasoning to say whether or no an alternating current arc could ever be obtained of an efficiency equal to that of the direct current arc. With suitable carbons, length of arc, current, and volts, it seemed to him that it might be possible to obtain an equal efficiency. The light-giving process in an arc is not merely an irreversible degradation of electric energy into heat; for the difference of potential between the carbons may be written $V = a + bl$; where a may be regarded as a back electromotive force, and bl as a true resistance. The first term of this expression does not vary with the length of the arc (l), but the second term does. Multiplying through by the current (C), the equation—

$$\text{Watts expended} = Ca + Cbl$$

is obtained. It is the first of the terms on the right-hand side, which is a reversible effect, and corresponds to the power expended in driving the current against a back electromotive force, on which the light given out chiefly depends, due to something occurring at the crater surface.

Mr. BLAKESLEY asked whether Prof. Thompson's idea of the light being due to the reversible part of the process was not a strong argument in favour of the direct current arc.

Prof. AYRTON said that in two communications made to the Congress held at Chicago it was shown that even with direct-current arcs there was a certain length of arc for which the efficiency was a maximum. Mrs. Ayrton had quite recently found that the efficiency of arc lamp carbons altered with time. Prof. Thompson's suggestion as to a thermic lag was a valuable one.

Prof. FLEMING, in his reply, said that when comparing two agents where there were so many variables, it was practically necessary to restrict the investigation. In their case they had kept the mean power constant and had left the other variables to take care of themselves.

The Society then adjourned till March 13th.

EDINBURGH UNIVERSITY CHEMICAL SOCIETY.

Fifth Ordinary Meeting, January 27th, 1896.

DR. DOBBIN read a paper on "*Scheele as a Chemist.*"

This paper, which is incapable of abstraction, was a discussion of Scheele's paper on the "Colouring Principle of Prussian Blue."

Sixth Ordinary Meeting, February 10, 1896.

Mr. W. W. TAYLOR, M.A., read a paper on "*Chemical Theories.*"

Seventh Ordinary Meeting, February 24th, 1895.

Dr. J. E. MACKENZIE read a paper on the "*Metallurgy and Analysis of Copper,*" of which the following is an abstract.

Native copper is found in large quantities, notably near Lake Superior. The chief difficulty of working it is its occurrence in immense masses, these having to be cut through by chisel in order to be made portable.

The treatment of copper ores may be divided into three classes:—

- I. Of ores free from sulphur.
- II. Of ores containing sulphur.
- III. Of ores containing very small percentages of copper (3 per cent and under).

I. The minerals so worked are cuprite, malachite, and azurite. The two latter are found in large quantities in the Ural mountains; the finer varieties being used as ornamental stones. The metal is won from these ores by fusion with charcoal in a small blast furnace; the impure metal being refined by melting in a small furnace with hemispherical bed, a blast of air being directed on to the metal to oxidise the impurities.

II. The minerals here treated are copper pyrites (or chalcopyrite), bornite (or purple copper ore), copper glance (or redruthite), and indigo-copper; the first-mentioned being that most commonly used. The ores first undergo calcination in heaps, "stalls," kilns, or reverberatory furnaces.

The first two methods are somewhat wasteful, and only adopted where timber is abundant. Kilns are generally used for ores poor in sulphur. In the Swansea district reverberatory furnaces are mostly used. The temperature of the furnace is not raised so high that the ore fuses. In calcination, most of the As and part of the sulphur are converted into oxides, and carried off with the products of combustion. The calcined ore now undergoes the "melting" or "fusion" process, after mixing with "metal slag." The resulting product, known as "coarse metal," is granulated by running into water. It should approximate to the formula CuFeS_2 . The granulated metal is again roasted, the iron sulphide being converted into oxide. The "roasted coarse metal" is now fused with refinery slags, so that the iron is carried off in the slag as a silicate, and the copper separates as "white" or "fine metal." This should contain about 75 per cent Cu, and nearly correspond to the formula Cu_2S . It is then roasted; by which process sufficient Cu_2S is converted into Cu_2O , so that when melted they may react and form Cu and SO_2 . On fusion the reaction takes place with violent boiling. The crude copper is known as "blister" or "pimple copper" from its appearance, and it should contain about 95 per cent Cu. It is refined by melting and oxidation of the impurities, and then "poling" to reduce the copper which had been oxidised.

III. Burnt pyrites from sulphuric acid works frequently contain small amounts of copper. They are calcined with rock salt, by which means copper chloride is produced. By scrap iron, the copper is precipitated from its solution. The crude copper is purified as above, or by electrolysis. Certain ores, on treatment with dilute sulphuric acid, give up their copper as sulphate, which, in its turn, may be treated with scrap iron.

The ordinary methods of analysis were briefly mentioned, special emphasis being laid on the electrolytic.

Photographs obtained with the Röntgen Rays.—A. Isbert and H. Bertin Sans.—An account of certain photographs of diseased portions of the internal parts of the human system. No new principle is brought to light.—*Comptes Rendus*, cxxii., p. 384.

NOTICES OF BOOKS.

Practical Studies in Fermentation, being Contributions to the Life-History of Micro-Organisms. By EMIL CHR. HANSEN, Ph.D., Professor and Director at the Carlsberg Physiological Laboratory, Copenhagen. Translated by ALEX. K. MILLER, Ph.D., F.I.C., F.C.S., and Revised by the Author. London: E. and F. N. Spon, 125, Strand. New York: Spon and Chamberlain, Cortlandt St. 1896. 8vo., pp. 277.

WITHIN the recollection of persons still living, brewing was perhaps the very type of a rule-of-thumb trade. Experience and care in the selection of his materials often enabled the brewer to obtain satisfactory results, but he was always at the mercy of accidents. A variation in the quality of the water employed, of atmospheric influences, of the malt, and above all of the yeast, might at any time involve a failure as inexplicable as disastrous.

More correct views, involving a reform in practice, were initiated by Cagniard Latour, Schwann, Turpin, and Kützing. The nature of fermentation was scrutinised, and, in opposition to the view of Liebig, it was shown to be essentially a biological process. The high philosophic import of this result has made itself widely felt. It has thus been shown, in opposition to Comte and others, that the so-called simpler sciences cannot be constituted without the aid of those more complicated. In this task Pasteur took a most important part. It was shown to be a capital precaution that the yeasts employed should be "pure," i. e., free from the "wild yeasts" which set up so-called diseases in beer, and render it unsaleable. But how is the pure yeast to be regularly and constantly obtained? Pasteur's method—the addition of a solution of cane-sugar to which tartaric acid had been added—certainly suppressed the bacteria present in the yeast, but it proved unsuitable for the production of a good brewery yeast.

Our author shows that of the *Saccharomycetes* known, one species only gives a normal beer of a good flavour and odour. The species which he recommends is that now widely known as "Carlsberg bottom yeast, No. 1."

The disappointment experienced in breweries, and the occurrence of diseases in beer, are traced to the presence of foreign species which have gained entrance. The most dreaded of these intruders is *Sacch. Pasterianus* I., which gives a peculiarly unpleasant taste and disagreeable odour. A single species of yeast is able to effect the entire fermentation, and special secondary yeasts are not necessary. This has been fully proved in German breweries, both for top and bottom fermentation.

It must not be supposed that the activity of ferment-microbia is confined to beer. Leaving out of question wines, ciders, and fruit wines, all of which may be much improved by careful attention to the processes of fermentation which they undergo, and to the improvement which they may receive by the use of a pure and suitable yeast, we find that butters and cheeses, if to be of the best quality, must receive ferments of a faultless quality. Many German dairies have been supplied from Weigmann's laboratory with pure cultures of a bacterium which is employed for souring cream.

The principle has been introduced in the tobacco manufacture. According to Suchsland, of Halle, the ordinary tobacco can, by means of fermentation, be made to acquire a superior aroma, a change for which there was some little room.

In the preservation of vinegar we must not omit to mention that it is much improved by the application of heat—of course in an air-tight vessel. This method of treatment was devised by Scheele as early as 1782.

How long will it be before we discover all the merit of the unobtrusive Swedish chemist?

Pure yeasts are also advantageously employed in the manufacture of bread.

This work should be carefully studied by all persons who are concerned with fermentation processes.

Cyanide Processes. By E. B. WILSON, E.M. New York: John Wiley and Sons. London: Chapman and Hall (Ltd.). 1896.

COSTLY litigation has of late attracted no little attention to improved means of extracting gold from auriferous quartz, tailings, &c. Among such methods the cyanide process, in its various modifications, of course takes the lead. The author disclaims any attempt to criticise the mechanical arrangements for the process, as they must vary with local circumstances. He admits that, as early as 1806, the solubility of gold was mentioned by Hagen. But he holds that "it is of no special moment to us who discovered the process, or whose process or patent is valid; that McArthur's people proved the way by practical demonstration is of more value to the world than who owns the patent." Yet he points out that McArthur at first pronounced the intervention of oxygen in the process unnecessary, but afterwards repented. The credit of first applying electricity is given to Siemens and Halske, and the author insinuates that McArthur was afraid of the Siemens and Halske process when he accused the electric current of dissolving the base metals (p. 103). He asserts (p. 73) that neither McArthur and Forest nor Siemens and Halske "designed or produced anything new, but, having strength in their convictions, they applied their patents to obtain useful results." But, in addition to strength in their convictions, they had at their disposal the needful funds. Many inventors may have strong convictions, but cannot obtain the capital for their applications on a useful scale. The author holds that Siemens and Halske made two great improvements over the old process, viz., saving cyanide and zinc and trouble in refining.

Mr. J. B. Hannay's process (Hannay?) is pronounced an admirable plan to obtain all the good points. It is said to yield an average of 86.1 per cent.

The process of W. Crookes (Patent 462,535; 1891) is described at some length, with the comment that "it may be successful in the laboratory on rich ores, but we have never heard of it beyond the patent specification."

Apparently all the cyanide processes are described, but we do not see that a decided preference is ascribed to any. The index might with great advantage have been made more copious.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 6, February 10, 1896.

At this meeting of the Academy the President announced the death of Jules Reiset, a member of the section on Rural Economy.

Study of Uranium Carbide.—Henri Moissan.—To obtain this compound, the author takes 500 grms. of the green uranium oxide mixed with 60 grms. sugar charcoal, both in fine powder, and heats 800 grms. of this mixture, contained in a crucible of coke, in the electric furnace for eight to ten minutes, using a current of 900 ampères and 50 volts. In about five minutes the reaction is produced with an issue of electric sparks. The liquid carbon is allowed to solidify and cool in the furnace. It has a crystalline fracture. Its specific gravity, taken in benzene, at 18° is 11.28. It scratches rock crystal, but not corundum.

If pulverised without precautions, it takes fire. If slightly heated it is attacked by fluorine. At 350° it is attacked by chlorine, and at 390° by bromine. Hydrochloric, sulphuric, and nitric acids attack it slowly in the cold. Its composition corresponds to the formula C_3O_4 . Its behaviour with water enables us to obtain hydrogen carbides, both gaseous, liquid, and solid.

Action of Currents of High Frequency upon Bacterian Toxines.—MM. d'Arsonval and Charrin.—Experiments proved that currents of high frequency attenuate the bacterial toxines. Toxines thus attenuated increase the resistance of animals into which they have been injected.

Application of the Rays of Röntgen to Surgical Diagnosis.—MM. Lannelongue and Oudin.—Already inserted.

Campholide: a Product of the Reduction of Camphoric Anhydride.—A. Haller.—This substance has the composition $C_{10}H_{16}O_2$. It is formed by reducing with sodium amalgam an alcoholic solution of camphoric anhydride, keeping the liquid acid by means of dilute sulphuric acid.

Influence of the Chemical Nature of Substances on their Permeability by the Rays of Röntgen.—Maurice Meslans.—Already inserted.

Application of Röntgen's Method.—Albert Londe.—Already inserted.

Increase of the Photographic Yield of the Röntgen Rays by means of Phosphorescent Zinc Sulphide.—Charles Henry.—Already inserted.

Photographic Proofs obtained by means of X Rays.—Ch. V. Zenger.—Already inserted.

Mechanical Action emanating from Crookes Tubes analogous to the Photographic Action Discovered by Röntgen.—MM. Gossart and Chevalier.—Already inserted.

Copper Silicide.—M. Vigouroux.—Copper silicide is a very hard brittle substance, of a steel-grey, if recently fractured, but gradually assuming a reddish aspect. Its specific gravity at 18° is 6.9. Its composition is represented by the formula $SiCu_2$.

Thionyl Chlorobromide and Bromide.—A. Besson.—This paper is not adapted for useful abstraction.

Crystalline Tin Sulphophosphide.—A. Granger.—A blackish grey substance, insoluble in hydrochloric and nitric acids, and in aqua regia. When in a fine powder it dissolves readily in a solution of potassa or soda through which a current of chlorine or bromine is being passed.

Zinc Oxyiodides.—M. Tassily.—The author describes three of these compounds:— $ZnI_2, 9ZnO, 24H_2O$, $ZnI_2, 5ZnO, 11H_2O$, and $3ZnI_2, 5NH_3, 3H_2O$.

Determination of the Purity of Butter by means of its Specific Gravity.—Raoul Brullé.—The author shows the necessity of eliminating all water by means of appropriate desiccating agents, simple fusion being insufficient, as well as the colouring-matters and the caseine.

No. 7, February 17, 1896.

Preparation and Properties of Cerium Carbide.—Henri Moissan.

Lithium Carbides.—Henri Moissan.—These two memoirs will be inserted in full as early as possible.

Lowering of the Explosive Potentials, Static and Dynamic, by the X Rays.—R. Swyngedauw.—(See p. 109).

Electrical Phenomena produced by Röntgen's Rays.—A. Righi.—(See p. 109).

Action of Röntgen's Rays on Electrostatic Rays, and the Striking Distance.—J. J. Borgman and A. L. Gerchun.—(See p. 110).

Photographic Researches on the X Rays.—Auguste and Louis Lemière.—This paper will be inserted *in extenso*.

Experiments showing that the X Rays emanate from the Anode.—M. de Heen.—In order to take date, I have the honour to bring to your knowledge that, according to my last experiments, the X rays of Lenard and Röntgen emanate, not from the kathode, but from the anode. To demonstrate this, it is sufficient to place between the Crookes tube and the sensitive plate a screen of lead pierced with some apertures permitting the passage of bundles of rays. The direction of these on the plate shows that they emanate from the positive and not from the negative pole. They are therefore *anodic* rays.

Photographic Proofs obtained in Darkness.—A. Besançon.—I have the honour of submitting to the Academy two photographic proofs obtained under the following circumstances:—On the glass of a frame for positives I applied a leaf of black cardboard, covering it completely. Upon this leaf I arranged two sensitive plates, above which I placed a twig of cypress and a fish put up in a sheet of black cardboard; above all, a bed of blotting-paper. Then I closed the frame with its lid. The whole was wrapped up in several thicknesses of black cloth. These operations were performed in the camera. I then deposited the packet in a box hermetically closed in a room well closed. I had thus darkness as complete as possible. Two hours afterwards, I developed the proofs, and obtained the result which may now be seen. In my idea, this experiment was intended to verify a hypothesis which would explain the transmission of light through opaque bodies. All substances allow themselves to be saturated with the luminous rays; when once saturated, they give off the light which they have received, and can thus act in darkness upon a sensitive plate. The result of my experiment does not seem to fully confirm this hypothesis; for the negative image of the object, instead of being light, ought to be black. Perhaps further experiments may give the explanation of this apparent anomaly. However this may be, a body which has been exposed to light impresses a sensitive plate in darkness.

Rapid Process for the Determination of Arsenic.—R. Engel and J. Bernard.—This paper will be inserted in full.

Practical Synthesis of Geranic Acid. Constitution of Lemonol and Lemonal.—P. Barbier and L. Bouveault.—This partial synthesis of geranic acid distinctly shows the accuracy of Tiemann's formula. This modification of the formulæ of lemonol and lemonal involves likewise the modification of those which we have proposed for licareol and licarhodol.

Certain Derivatives of Eugenol.—Ch. Gassmann.—An account of eugenolacetic acid, of isoeugenolacetic acid, and of vanilline acetic acid.

Composition of Fire-damp.—Th. Schloësing, jun.—We may generally, in practice, regard the combustible portion of fire-damp as consisting simply of methane. It may, however, comprise a proportion—small, but appreciable—of the hydrocarbons.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd inst., Sir James Crichton-Browne presiding. The following were elected Members:—H. J. Allcroft, R. L. Andrews, Dr. Ernest Clarke, F.R.C.S., Mayo Collier, F.R.C.S., H. E. Fry, Mrs. Francis Gaskell, E. Gillingham, A. Glegg, Sir Cameron Gull, Bart., M.P., Miss Catherine Imray, C. W. Keighley, Dr. Edward Law, M.R.C.S., C. Letts, M. Micholls, R. E. Middleton, M.Inst.C.E., Dr. A. Paine, G. H. Sykes, M.Inst.C.E., and W. L. Wise, J.P.

The City and Guilds of London Institute.—The Executive Committee have awarded the second Salters' Company's Research Fellowship for the encouragement of Higher Research in Chemistry in its relation to Manufactures to Sidney Williamson, Ph.D., F.I.C., F.C.S., who was for two years a student at the City and Guilds Technical College, Finsbury, and subsequently for three years at the City and Guilds Central Technical College. The Fellowship is tenable at the latter, and Dr. Williamson proposes to work on some questions bearing on food-stuffs generally, more particularly the examination of some definite albumenoids, with the ultimate object of ascertaining the influence of various manures on the growth of crops in so far as *quality* of produce is concerned.

MEETINGS FOR THE WEEK.

MONDAY, 9th.—Medical, 8.30.

TUESDAY, 10th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.

— Society of Arts, 8. "English Book Illustration, 1860—70," by Joseph Pennell.

— Medical and Surgical, 8.30.

— Photographic, 8.

— Institute of Civil Engineers, 8.

WEDNESDAY, 11th.—Society of Arts, 8. "Peasant Life and Industries in Ireland," by Prof. A. C. Haddon.

— Geological, 8.

— Pharmaceutical, 8.30.

THURSDAY, 12th.—Royal, 4.30.

— Mathematical, 8.

— Institute of Electrical Engineers, 8.

— Royal Institution, 3. "Masters of Modern Thought—II. Rousseau," by The Rev. W. Barry, D.D.

FRIDAY, 13th.—Royal Institution, 9. "The Theory of the Ludicrous," by W. S. Lilly, M.A.

— Physical, 5. "An Addition to the Wheatstone Bridge for the Determination of Low Resistances," by J. H. Reeves.

— "On Kathode Rays," by Herr Paley.

SATURDAY, 14th.—Royal Institution, 3. "Light," by Lord Rayleigh, F.R.S., &c.

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Only in exceptional cases and by payment of an additional fee can applications be received from Local Secretaries after that date.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1894.

ON THE ACTION OF THE X RAYS UPON
THE DIAMOND.

By ABEL BUGUET and ALBERT GASCARD.

THE transparency of the different varieties of carbon and of its non-metallic compounds, established by Professor Röntgen and then by the experimentalists who have studied the X rays, may serve to distinguish clearly the diamond from its imitations made of very opaque substances.

The proofs which we have the honour to submit to the Academy show in juxtaposition silhouettes of genuine diamonds and of imitations both loose and set. Prolonged exposure soon succeeds in causing the silhouettes of genuine diamonds to disappear, whilst false diamonds continue to behave like opaque substances. The same procedure has also allowed us to distinguish natural jet from its mineral imitation.

In addition to this graphic method we have tried an optical method, in which we have tried the fluorescence studied by Prof. Röntgen. Diamond and jet, if interposed between the Crookes tube and a leaf of paper covered with a fluorescent substance (e.g., barium platino-cyanide), project upon the paper shadows lighter than those which appear beneath imitations placed near.

Here then we have two very certain tests: the *graphic* method leaves an irrefutable document, whilst the *optical* method is instantaneous. They will easily come into practical use, since a precious stone may be tested even in its setting, and without running any risk.—*Comptes Rendus*, cxxii., p. 457.

ON CERTAIN PROPERTIES OF DARK LIGHT.

By GUSTAVE LE BON.

DARK light seems, as I have indicated, to consist of a spectrum of very different rays, whence the term dark light must be considered as applicable to all the radiations invisible to the eye, but visible to the photographic plate or to any instrument.

Organic substances are generally easily traversed by the cathodic rays, and very badly by dark light. Hence we can only photograph the bones with the cathodic rays, since all the other parts are as transparent to these rays as crystal is to solar light.

As dark light traverses organised substances unequally and with difficulty, we may perhaps succeed in photographing the various layers of certain tissues. I have the honour of submitting to the Academy photographs of frogs taken with dark light. They still show only the more superficial parts of the animal. They have been taken in an ordinary frame between a polished copper plate and a sheet of lead, the whole exposed to the light of day. The interposition of a plate of glass between the sensitive surface and the animal does not prevent the formation of the image, but causes it to lose much of its distinctness, as would be the case with the reproduction of any proof.

I will add, according to my most recent researches, that certain organised beings appear to have the property of emitting, in dark places, radiations of dark light capable of acting on photographic plates. I submit to the Academy the photograph of a frog produced in complete darkness, merely by placing it for two hours on a sensitive plate in a frame. The parts reproduced differ,

however, from those obtained in the foregoing experiment.

Not all organised bodies can be thus reproduced. The living human hand, exposed for an hour and a half upon a sensitive plate in darkness, gives no trace of an image if it has been perfectly cleansed.

It might be objected, to the experiment of the reproduction of the frog in darkness, that the reduction of the silver salts constituting the image is due to chemical compounds present in the viscid liquid with which the animal is coated, and, in fact, the interposition of a plate of glass between the sensitive plate and the body of the frog prevents the appearance of the image. But the image is still formed if the viscid matter is removed by steeping the animal for some hours in alcohol at 90°. I cannot therefore decide exactly upon the interpretation of the results of this experiment.

There does not seem to exist any analogy between the phenomena just described and those called condensed light. Numerous experiments have convinced me that the majority of bodies do not possess the property of acting upon sensitive plates in darkness.—*Comptes Rendus*, cxxii., p. 462.

ON A RAPID PROCEDURE FOR THE
DETERMINATION OF ARSENIC.

By R. ENGEL and J. BERNARD.

THE determination of arsenic, especially when small quantities are concerned, presents difficulties and causes of uncertainty, and always requires a considerable time.

With a view to biological researches, A. Gautier (*Bull. de la Soc. Chim.*, xxiv., p. 251) has studied the determination of arsenic by weighing the ring obtained by Marsh's method, and has carefully studied the conditions which must be observed to avoid any loss. This process, in the hands of the author and of one of his pupils, has given the most accurate results, but its application is very delicate, and its duration is rather long for ordinary determinations of arsenic.

The following procedure, disregarding the time of precipitation, requires only a few minutes, and gives very accurate results.

The principles on which it depends are as follows:—

1. The oxygen compounds of arsenic in solution in concentrated hydrochloric acid are entirely reduced by hypophosphorous acid to the state of non-metallic arsenical compound, as appears from the earlier experiments of one of us.
2. Iodine in solution transforms non-metallic arsenic (i.e., arsenic in combination with a non-metallic element) into arsenious acid, with the formation of merely small quantities of arsenic acid as long as the liquid remains acid. In a liquid rendered alkaline by bicarbonates the transformation into arsenic acid is total.

The procedure is carried out as follows:—

To an arsenical solution brought to 20 c.c. or 40 c.c. by concentration in an alkaline solution, if needful we add three times its volume of hydrochloric acid at sp. gr. 1.169, and then a large excess of hypophosphorous acid; according to the presumed quantity of arsenic, we use from 4 to 10 c.c. of a solution of this acid at 1.299 sp. gr. The precipitate at ordinary temperatures appears as a brown powder. It is well to operate in a vessel of the shape of a truncated cone, with a ground glass stopper.

After standing for about twelve hours, the mixture is gently heated in the water-bath. We add an equal volume of boiled water, still boiling: this operation is to facilitate the precipitation, which is more rapid with hot liquids.

The clear liquid is first filtered, and the precipitate is then brought upon the filter. We wash the vessel and

the precipitate with boiling water, without regarding a very slight deposit which sometimes adheres to the vessel. We wash until the filtrate is no longer acid. The filter containing the precipitate is then returned to the vessel in which the precipitation was effected, and we add gradually, from a graduated burette, a decinormal solution of iodine, with continual stirring. The first quantities of iodine are rapidly decolourised. As only three-fifths of the total iodine necessary to transform the arsenic into arsenic acid are consumed in dissolving the arsenic, we may, after each decolouration, add at once rather more than half the volume of iodine without risk of adding excess. It is essential not to add water at this stage of the operation, in order that the solution of iodine may remain sufficiently concentrated to react rapidly.

When after a last addition the liquid remains coloured, we wait two or three minutes, stirring from time to time, so as to dissolve the last traces of arsenic adhering to the filter or to the glass. We add then about 50 c.c. of water and 10 c.c. of a saturated solution of sodium bicarbonate. This addition determines the immediate decolouration of the liquid and of the fragments of the filter.

We complete the titration with iodine, using starch as indicator, as in the well-known titration of arsenious acid by iodine. Each c.c. of iodine employed corresponds to 0.0015 gm. of arsenic.

This determination may be effected in presence of all the metals of the third, fourth, and fifth groups.

Here follow the results of some analyses in which known quantities of arsenious acid have been added to saline solutions of the following metals:—

Metal along with arsenic.	Arsenic added.	Arsenic found.
Nickel	0.054	0.0539
Cobalt	0.074	0.0735
Manganese ..	0.059	0.0589
Aluminium ..	0.084	0.084
Zinc	0.123	0.1229

As 1 c.c. of decinormal solution of iodine corresponds to 1.5 m.grm. of arsenic, we see that it is possible, without an appreciable error, to determine 1/10th m.grm. with ordinary burettes.—*Comptes Rendus*, cxxiii., p. 390.

ON THE NATURE OF AN OXIDISING SUBSTANCE PRODUCED BY DISTILLING AQUEOUS SOLUTIONS OF POTASSIUM PERMANGANATE AND SULPHURIC ACID IN VACUO.

By COLIN C. FRYE.

SOME years ago, it was found by Dr. Collie that when solutions of sulphuric acid and potassium permanganate of certain strengths were distilled *in vacuo*, the distillate liberated iodine from potassium iodide. It is also given in some text-books that ozone can be prepared in this manner, and it was to prove this that this investigation was carried out.

The substance that liberated iodine might possibly have been any of the following:—Persulphuric acid, permanganic acid, peroxide of hydrogen, or ozone.

The first thing to do was to find out what strength of solution gave most of this substance, or liberated most iodine; and about thirty experiments were carried out for this purpose. Great care was taken to avoid splashing of any kind, as this, of course, would have vitiated the result.

A mean of 0.008602 gm. of iodine was liberated in these experiments. No iodine was liberated from solutions of under 22 per cent strength of both sulphuric acid and potassium permanganate. After this, iodine was

liberated up to 50 per cent strength of both solutions, above which strength large quantities of oxygen were evolved. The iodine-liberating agent in the distillate decomposes completely in about fifteen minutes.

For Peroxide of Hydrogen.—The distillate was mixed with a solution of sulphuric acid and potassium bichromate, and then shaken with ether. No blue colour was imparted to the ethereal layer, but it was afterwards found that this test does not work with solutions so dilute as this one might have been. Also, no peroxide of hydrogen could be detected by the extremely delicate titanous acid test recommended by Mr. A. Richardson (*Journ. Chem. Soc.*, 1893, p. 1110).

For Persulphuric Acid.—Sixteen distillations were made, and the collected distillates allowed to decompose and then precipitated with barium chloride, but only 0.001 gm. of barium sulphate was obtained; whereas, if it had been persulphuric acid, and had decomposed into sulphuric acid and water, one ought to have got about 0.3000 gm. of barium sulphate (calculated by the iodine liberated from each).

For Permanganic Acid, or a Manganese Compound.—The substance was distilled through a red-hot tube, and then conducted into a solution of potassium iodide. No iodine was liberated, and no deposit of any manganese compound was perceived on the cooler portion of the tube.

Ozone.—The distillate before condensation was passed through a warm tube containing manganese dioxide, when it did not liberate iodine; but when the manganese dioxide tube was omitted, it both liberated iodine from potassium iodide, and also had a slight action on mercury, when collected over it, oxygen being found.

From the above experiments it appears evident that the oxidising agent which is made by the action of sulphuric acid on potassium permanganate is ozone; but it is rather difficult to explain the fact that ozone should dissolve so readily in water, when the pressure is reduced to only about one-half to one inch of mercury; ozone prepared by sparking oxygen being very slightly soluble in water at ordinary pressures.

Chemical Laboratory, University College,
January 28, 1896.

THE DEPOSITION OF ALUMINIUM FROM AQUEOUS SOLUTIONS.

By H. N. WARREN, Research Analyst.

THE divers assertions put forth by various authors as regards the deposition of aluminium are not only fabulous, but in many cases alchemical.

In an exhaustive work on electrotype manipulation by Charles V. Walker, F.R.S., &c., the author claims to be able to produce aluminium from the decomposition afforded by the aid of three Smee's batteries; employing as a depositing solution, one obtained by incorporating pipe-clay with sulphuric acid. The same author further states that the metal may be readily detached from the electrode, if desired, as fast as deposited. Granting that this be both an inexpensive and at the same time ready method for the formation of that substance, how comes it that this method is not commercially employed?

During the past twelve months, various trials have been made at this laboratory with a view to ascertain the possibility of obtaining a deposit from aqueous solutions; and, among other methods, consisting in the decomposition of cyanides, sulphocyanides, sulphides, and various other aluminous compounds, was attempted the decomposition of kaolin, as before stated. In this case the writer also obtained the white deposit formerly referred to, but which upon verification is found to be readily soluble in acids, perfectly magnetic, and affords a

deep blue colouration upon the addition of potassium ferrocyanide, evidently aluminium-iron. After all, it is possible, but very difficult, to deposit aluminium from its aqueous solutions, and the author advises the following solution:—Dissolve aluminium hydrate in HCl, add a large excess of tartaric acid, and, lastly, an excess of ammonia, until a clear ammoniacal solution is obtained. Aluminium may be deposited by a current of 12 volts 9 ampères; employing metallic aluminium as a positive, and a sheet of brass as a negative electrode. Or replacing the positive with carbon, the deposit thus obtained in either case is perfectly white, and will bear burnishing; but, strange to say, after once covering the surface of the negative plate, a further deposit is considerably retarded, which can only be effected by further increasing the negative plate from this solution.

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ON THE VOLUMETRIC DETERMINATION OF TITANIC ACID AND IRON IN ORES.

By H. L. WELLS and W. L. MITCHELL.

THE difficulties connected with the gravimetric determination of titanic acid make a reliable volumetric method very desirable, especially for the analysis of titanic iron ores. We have therefore turned our attention to this subject, and have found that satisfactory results can be obtained by a slight modification of a process which has long been known.

About thirty years ago F. Pisani (*Comptes Rendus*, lix., 289) stated that the acid under consideration could be determined by reduction with zinc in hydrochloric acid solution, using a gentle heat, and when the violet colour no longer deepened, pouring off the liquid from the remaining zinc and titrating with potassium permanganate. Pisani gave no test analyses, and, since his process has not been generally adopted, it is evident that it has not proved satisfactory in the hands of others.

A number of years ago one of us (Wells) had occasion to analyse a large number of titanic iron ores, and attempted to use Pisani's method with the use of sulphuric acid instead of hydrochloric acid, as recommended by the originator of the process. This modification was made on account of the well-known interference of chlorides with the permanganate method, and it was found that the difficulty mentioned by Pisani, that titanic acid was liable to be precipitated by heating sulphate solutions, could be readily overcome by using a sufficiently large quantity of sulphuric acid. The results of a great many trials at that time, however, showed that the method gave very low results, and the process was then abandoned. The process used in the experiments just referred to was precisely the same as that which we now recommend, and which will be described in detail below, except that after reduction with zinc the solution was poured off, from the excess of that metal, into a beaker for titration, an operation which Pisani recommended, and which is customary in the determination of iron by this method. It is now evident that the failure of the method was due to the contact of the solutions with atmospheric air, for, while ferrous sulphate is acted upon very slowly, the sulphate corresponding to the lower oxide of titanium is very rapidly oxidised under such circumstances.

Marignac (*Zeitsch. Anal. Chem.*, vii., 112), with his accustomed skill, applied Pisani's method, soon after its publication, to the determination of titanic acid in the presence of niobic acid. He was obliged to use special conditions in order to avoid the reduction of the other acid at the same time; but the feature of his process which is interesting in the present connection is, that he reduced the titanic acid by means of a long rod of pure

zinc extending up into the neck of the flask which held the solution, and, after allowing the reduction to take place out of contact with air, he finally took out the zinc and titrated directly in the flask without transferring. Marignac gave a number of test analyses which showed that the method gave very good results, although they were a little too low with the larger quantities of titanic acid used.

We have modified the method of Pisani as improved by Marignac, by using sulphuric acid solutions, and by protecting the liquid during cooling and titration by means of carbon dioxide, and we have also arranged the process for the determination of iron along with the titanic acid. The details of the operation are as follows:—

Five grms. of very finely pulverised ore are placed in a rather large beaker covered with a watch-glass, and treated with about 100 c.c. of concentrated hydrochloric acid. A very gentle, gradually increasing heat is applied for several hours, more hydrochloric acid is added if necessary, and, when no further action is apparent, about 50 c.c. of a mixture of equal volumes of concentrated sulphuric acid and water are added, and the whole is evaporated until the sulphuric acid fumes strongly. After cooling, about 200 c.c. of water are added, the whole is heated until the sulphates are dissolved, and the liquid is filtered into a litre flask. With many titanic ores this operation will have dissolved everything except siliceous matter. If, however, some undissolved ore remains, it is ignited, to burn the filter-paper, in a platinum crucible, and the residue is fused with potassium disulphate, at a gradually increasing heat, up to low redness, until the black particles have disappeared. To the cake in the crucible several volumes of concentrated sulphuric acid are added, heat is gradually applied until the whole becomes liquid, then this is heated with a moderate volume of water to dissolve the sulphates, and the liquid is added to the main solution in the litre flask. Filtration may be omitted here, or in the case of the original solution, provided that the siliceous matter is not to be weighed.

The liquid in the litre flask is diluted to the mark and mixed, and four portions of 200 c.c. each, representing 1 grm. of ore, are taken, two of them into Erlenmeyer (conical) flasks of 500 c.c. capacity, and the other two into ordinary flasks of 350 c.c. capacity.

To determine iron, hydrogen sulphide is passed into the solutions in the ordinary flasks until they are saturated with the gas, then inverted porcelain crucible covers are placed upon the mouths of the flasks, and the solutions are heated and boiled continuously, so that air cannot enter, until the hydrogen sulphide has been completely removed. This point can be determined by testing the escaping steam with paper which has been dipped in a solution of lead acetate made strongly alkaline with potassium hydroxide. The flasks are then quickly filled to the neck with cold distilled water which has been recently boiled, —best by means of an inverted wash-bottle, directing the stream against the neck of the flask in such a way that the water does not mix to a great extent with the heavier sulphuric acid solution. If the stream of cold water does not strike the top of the neck, there is little danger of breaking the hot glass. The contents of the flasks are now rapidly cooled by means of a stream of water, transferred to large beakers, and titrated with potassium permanganate solution.

To the solutions in the Erlenmeyer flasks about 25 c.c. of concentrated sulphuric acid are added; then in each case three or four rods of chemically pure zinc, about 50 m.m. long and 6 or 7 m.m. in diameter, are attached to the loop of a porcelain crucible cover, which is larger than the mouth of the flask, by means of platinum wire wound securely around them near the middle. The length of the wire is so arranged that the pieces of zinc will be suspended in the liquid when the cover is placed on the flask. When this has been accomplished the liquid is boiled gently, so as to keep out air, for thirty or forty

minutes; then, without interrupting the boiling, a glass tube, so bent that it extends 50 m.m. or more into the flask, which is delivering a rather rapid stream of carbon dioxide, is introduced under the cover. Care should be taken to have the carbon dioxide free from air, and that hydrochloric acid which contains sulphur dioxide is not used for its generation. The flask is now rapidly cooled, and then the zinc is washed with a jet of water and removed, and the solution is titrated with permanganate in the flask while the carbon dioxide is still being passed in. The difference between the permanganate used in this case and that used for the iron alone represents the amount corresponding to the titanous acid. The factor for metallic iron divided by 0.7 gives the factor for titanous acid (TiO_2).

When a 50 c.c. burette is used, the most convenient strength for the permanganate solution is when 1 c.c. is equal to about 0.014 gm. of metallic iron, corresponding to 7.1% grms. of potassium permanganate per litre.

It is customary in this laboratory to standardise permanganate solutions by a method which very closely approaches the one described above for the actual determination of iron, so that, if any slight errors are inherent in the process, they are likely to be eliminated, because they have an equal effect upon the standardisation and the determination. The method is simple and convenient, and a large amount of experience has shown it to be very accurate. To carry out this operation, a 350 c.c. flask is half-filled with sulphuric acid (the strong acid diluted with about 8 volumes of water). This is heated to boiling with an inverted crucible cover upon the mouth of the flask, and, after the air has been expelled, about 6/10ths gm. of the purest iron wire, representing nearly the average amount of iron in 1 gm. of an ore, is dropped in, and gentle boiling is continued until it has dissolved. The flask is filled to the neck with water, cooled, and finally the liquid is transferred to a beaker and titrated.

The method of determining iron by reduction with hydrogen sulphide, although well known, does not appear to be as generally used as it deserves to be. The precipitated sulphur present in the liquid has absolutely no effect upon cold permanganate solution; but precipitated sulphides, such as copper sulphide, should be filtered off before boiling. Since concentrated sulphuric acid is an oxidising agent, care must be taken to use sufficiently dilute solution, and not boil them down until the acid becomes strong.

We have made some test analyses upon the method of determining titanous acid volumetrically. Crude potassium titanofluoride, K_2TiF_6 , was re-crystallised twice from water, and used as the source of titanium. Weighed quantities of the carefully dried salt were evaporated with sulphuric acid, and the resulting substance was treated essentially as has been described above, but with some variations in the time of boiling, the strength of the acid, and the amount of zinc used. The following table gives the results obtained in grms.:

Potassium titanofluoride taken.	Titanium found.	Titanium calculated.	Error.
0.7638	0.1437	0.1527	-0.0090
0.6425	0.1225	0.1285	-0.0060
0.7778	0.1524	0.1555	-0.0031
0.6793	0.1308	0.1358	-0.0050
0.8226	0.1607	0.1645	-0.0038
1.0956	0.2107	0.2191	-0.0084
0.4451	0.0848	0.0890	-0.0042
0.6359	0.1215	0.1271	-0.0056
0.9004	0.1715	0.1800	-0.0085
0.4634	0.0882	0.0926	-0.0044

The results show a fair degree of uniformity, but they are invariably too low. A part of the deficiency was probably due to the impurities in the potassium titanofluoride used, for it is quite possible that certain impurities may have been increased rather than diminished by re-crystallising it, and it is exceedingly difficult to obtain any tita-

nium compound that is certainly free from all other acid-forming elements. The greater portion of the error was doubtless due to the action of air which gained access to the liquid in spite of the precautions used, and it is evident that the accuracy of determinations made by this method would be increased by adding one-twentieth or one-thirtieth to the amount of titanous acid found under the conditions that we have used.

The great influence of the action of air is shown by two determinations which were made exactly like those given in the above table, except that, after cooling in carbon dioxide, the solutions were transferred to beakers and titrated as quickly as possible.

Potassium titanofluoride taken.	Titanium found.	Titanium calculated.	Error.
0.6831	0.1078	0.1366	0.0288
0.9545	0.1535	0.1909	0.0374

The volumetric method, even without correction, will be likely to give more reliable results than those obtained by gravimetric determination, unless great care and skill are displayed in carrying out the latter. — *Journal of the American Chemical Society*, xvii., p. 878.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 114.)

The Electric Spectrum of Chloride of Calcium.—I found the chloride spectrum, when using a spark without a condenser, the same as that described by M. Bunsen; there were neither more nor fewer lines than those drawn by the illustrious Heidelberg chemist in the plate accompanying his paper on the *spark spectrum*.

For these researches I used in succession the Steinheil and Duboscq spectroscopes, the latter fitted with *three* or *five* prisms. I proved the identity when examining one by one all the lines and the position of each of them. I varied the strength of the sparks from *one to five times* in intensity. The result, both as regards the *number* and *position* of the calcium lines, was always the same; the only change was in the intensity of the lines and in the non-appearance or appearance of air-lines.

When using a coil with a condenser, capable of giving sparks 15 c.m. long, but which was used for giving sparks only 3 m.m. long by adjusting the platinum balls, covered with fused chloride of calcium, and either wetted or not with a saturated solution of this compound, or when sparking from the surface of an acid solution in the apparatus* previously described, I could not find the *double blue line* at 148 to 149 divisions on my Steinheil spectroscope in the calcium flame spectrum, whereas I saw the *first blue line*, very deeply coloured, in the same position that it occupied in the flame spectrum. I have no hesitation in saying that the double blue line does not belong to the electric spectrum of calcium. It is more than doubtful if it is one of the specific lines of the oxyhydrogen calcium spectrum, although Sainte-Claire Deville, Debray, and I have frequently seen it when working with a pure lime crucible raised to white heat in an oxyhydrogen blowpipe.

It is well known that the flame and electric spectra described by M. Bunsen are different. My observations, checked by means of a spectroscope of the same design as that used by M. Bunsen, confirm this fact. For instance, in an oxyhydrogen blowpipe, oxide, chloride, and oxychloride of calcium show green bands and lines at 52 to 53 and at 60 to 61.5 divisions on the Steinheil spectroscope, corresponding to 55 to 56 and 61.5 to 63 divisions on the Bunsen spectroscope. These bands and lines are

* See CHEMICAL NEWS, vol. lxxii., p. 248.

entirely absent from the spark spectrum of chloride in a hydrogen atmosphere; but, on the other hand, the lines at 58, 68, and 68.5 divisions on the Steinheil spectrocope, which occur in the electric spectrum, are entirely wanting in the calcium spectrum in an oxyhydrogen or oxy-coal-gas blowpipe, whatever part of the flame be examined.

Each spectrum has its own appearance, whether it be considered *separately* or by *superposition*. The *oxyhydrogen* calcium spectrum is unchangeable, and, notwithstanding the coincidence of certain of its bands and one line, it cannot be made to coincide with the *electric* calcium spectrum.

The above observations and the conclusions I arrived at date from seven to eight years ago, as I said in the first chapter; since those researches were carried out, I have again converted oxide of calcium into chloride, both by pure dry hydrochloric acid gas, sheltered from air, and by the action of heat on a mixture of pure oxide of calcium and chloride of ammonium, in the air. Whilst carrying on all the operations in closed platinum vessels, I failed every time to procure platinum balls covered with chloride of calcium fused in the air, which would not show the sodium line when analysing a spark flashed in air or hydrogen.

I beg to refer any reader who wishes for details of these facts to the preceding chapter.

I used samples of exceptionally pure chloride to obtain a spectrum, both in an oxyhydrogen blowpipe and in an induction spark, working in air or in a hydrogen atmosphere.

When using Steinheil and Duboscq spectroscopes, I found in an oxyhydrogen blowpipe, after the dissociation of the chloride and the formation of oxychloride, the flame spectrum of oxide of calcium did not show even a momentary trace of the sodium line.

When making, by means of a Duboscq spectrocope with three or five prisms, or a large Hilger spectrocope with three prisms of Iceland spar, an analysis of an electric spark or discharge saturated with chloride in an atmosphere of pure hydrogen, I once more found the extreme accuracy of M. Bunsen's description.

The flame and electric spectra of chloride of calcium differ both in the *number* and *position* of their component lines.

The oxyhydrogen calcium spectrum alone shows a *single really sharp line*,—the blue line at 125.5 on the Steinheil, or 155 on the Bunsen, spectrocope. The other lines consist of more or less diffuse bands, and are not capable of being resolved by the instruments at my disposal. Every line in the electric spectrum is sharp, excepting *two or three at most*. The exceptions consist of groups of very close lines, which my instruments are not capable of separating.

With the object of satisfying myself as to the permanence of the number and position of the lines in the electric spectrum of calcium, I examined the arc spectrum of calcium under various conditions.

For this purpose I made an electric arc charged with calcium by means of a battery of *thirty* of the largest Bunsen cells, using pure carbon electrodes. The negative electrode, 10 c.m. long by about 5 m.m. diam., ended in a point which was coated with freshly-made fused oxychloride of calcium; the positive electrode, 10 c.m. long by about 1 c.m. diam., ended in a flat surface with a cavity. The flat rim was coated, and the cavity was filled with freshly-made oxychloride of calcium. The electrodes, arranged *vertically*, were inserted into strong *insulated* brass rings, working, by means of racks, on a varnished glass rod.

Having put the electrodes in contact, I formed the arc by heating the point of contact, and melting the oxychloride of calcium by means of a hydrogen and air blowpipe. I made observations, on the one hand, of the electrodes covered with oxychloride in contact, and, on the other hand, of the electrodes covered with oxychloride separated by the interval forming the arc.

As analysers, M. Rommelaere and I used in succession:—

1. The Steinheil spectrocope;
2. The Duboscq spectrocope, fitted either with three or five prisms;
3. The large Hilger spectrocope, fitted with three or six Iceland spar prisms.

Whatever spectrocope we used, the results were the same, as regards the calcium spectrum, when the electrodes were in *contact* and when they were separated,—that is to say, when we observed the arc properly so called.

Spectrum analysis of the incandescent part of the electrodes in *contact* showed a very bright continuous spectrum, with broad lines, so diffuse that it was impossible to decide whether they were due to a flame spectrum or to an electric spectrum, or to a mixture of the two spectra. The simple blue line was extremely sharp; the two broad, indistinct, deep red and yellowish red lines were the same as in the discharge spectrum.

On separating the electrodes, so as to form an *arc*, and looking exclusively at the middle of the arc, I saw a continuous spectrum, showing both the electric spectrum of calcium and the carbon spectrum in the form of *fine* lines, produced by the resolution of the carbon bands; the *two red calcium lines* were broad and hazy, but less so than in the spectrum made with the electrodes in contact. The luminosity in the arc was evidently greater.

I did not see in the arc spectrum the two blue lines seen in the spectrum of the *inner cone* of an oxyhydrogen and oxy-coal-gas blowpipe charged with calcium.

By putting chloride of calcium into the cavity in the positive electrode as it was volatilised, by means of a small spatula of pure carbon, I was enabled to reproduce the two spectra mentioned above *at will*, and for as long a time as was required for the observations, changing one spectrocope for another.

At the instant of introducing chloride of calcium into the arc, both M. Rommelaere and I always saw the sodium D line in the spectrum; but after a few moments it was scarcely more visible than in an arc without calcium passing in the air of the large room we were working in.

I found that an electric arc *charged with calcium* was quite *blue*; the envelope of the arc was bluish white, but above the arc I observed that deep brown colour characteristic of flames charged with pure calcium compounds at a high temperature.

Throughout these observations I saw no air lines, even when separating the electrodes so far as to break the arc.

When revising the spectroscopic researches described above, in collaboration with M. Depaire, we found that every observation was perfectly accurate, both for the flame spectrum and the electric spectrum of calcium.

It is undeniable that the flame and electric spectra of chloride of calcium are different, and that, by the means known to us, it is impossible to change the one into the other.

To satisfy ourselves as to the permanence of the electric spectrum of calcium, M. Depaire and I employed the powerful currents used for examining the electric spectrum of lithium.

For this purpose we formed an electric arc successively:—

1. By means of a battery of thirty-three Julien accumulator cells, giving at the terminals 10 ampères and 70 volts;
2. By means of a Gramme and Siemens dynamo coupled. Instead of a Foucault regulator we used a Gerard regulator, which gave a steadier arc than the former.

The pure carbon electrodes, coated with oxychloride of calcium, were arranged in the same way as described for the researches on the electric arc charged with lithium.

One of us used at first a Duboscq spectrocope, similar to that used by M. Lecoq de Boisbaudran; and after-

wards a Hilger spectroscope with two half-prisms and lenses of quartz; whilst the other used a new direct vision spectroscope with flint-glass prisms, designed by Messrs. Living and Dewar.

Having put the electrodes in contact, and completed the circuit by melting the oxychloride with a hydrogen and air blowpipe, we found, both with the current from the accumulators, forming an arc about nine m.m. long by eight m.m. diam., and with the current from the coupled dynamos, forming an arc about two and a half c.m. long by eight m.m. diam., the spectra were the same as those seen with the current produced by thirty Bunsen cells; that is to say, that spectrum analysis of the bright light, formed whilst the electrodes coated with chloride were in contact, showed a continuous spectrum, on which was superposed a calcium spectrum so diffused that it was impossible to define it, and that analysis of the arc proper showed a continuous spectrum, on which was superposed simultaneously the calcium spectrum of an electric discharge and a carbon spectrum as seen in an arc passing between pure carbon electrodes. In both cases the red lines are diffused, but very much less in the arc spectrum than in the induction spectrum; the diffused lines will probably be eventually resolved into fine lines.

The sodium D line *always* appeared in the chloride spectrum as soon as the arc was formed; but, after a few moments, this line became fainter, and at last appeared only as clearly as it was seen in an arc in the same atmosphere, and with the same recently heated electrodes.

In the calcium arc formed by the two coupled dynamos, the length of which was about 2½ c.m., the arc proper was coloured blue, the lower part of its envelope white, and the upper part of its envelope chocolate-brown.

However quickly the chloride of calcium occluded sodium from the medium in which it was made and kept, there was no connection between the luminous spectra of sodium, potassium, and lithium, and flame spectrum of oxide or chloride of calcium, and the electric spectrum of this last chloride.

It is impossible, by raising the temperature, to change the flame spectrum to the electric spectrum, and *vice versa*. Under the conditions in which I carried on my researches, these two spectra are unchangeable; they are specific, in the same degree and under the same conditions, as the spectra of sodium, potassium, and lithium.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, February 20th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. Jervis E. Foakes and C. E. Harrison were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Henry Thomas Durant, c/o Messrs. Loewenstein and Co., Johannesburg, South Africa; Herbert Edwin Macadam, Adam's Chemical Co., Victoria Docks, E.; Charles H. Reissman, B.A., B.Sc., Saxony Villa, Oppidans Road, Primrose Hill, N.W.; James Edward Shum Tuckett, M.A., 14, Hyde Road, Eastbourne.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As *Vice-Presidents*—Professor James Dewar, F.R.S., and Professor W. A. Tilden, F.R.S., *vice* Dr. E. Atkinson and C. O'Sullivan, F.R.S.

As *Ordinary Members of Council*—Dr. Forster Morley, Dr. G. H. Morris, Mr. J. W. Rodger, and Professor Arthur Smithells, *vice* Professor H. Dixon, F.R.S., Mr. R. J. Friswell, Dr. Kipping, and Dr. W. P. Wynne.

Messrs. Bertram Blount, H. Brereton Baker, and Dr. J. Shields were appointed to audit the Society's accounts.

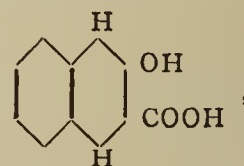
The following were duly elected Fellows of the Society:—

John Allan, William Henry Barker, B.Sc., William Henry Bentley, B.Sc., Maurice Blood, B.A., Joseph Edwin Algar Blyde, Joseph John Bowley, Herbert Lister Bowman, B.A., Daniel Bray, James Kerry Burbridge, Hugh Charles Herbert Candy, B.Sc., James Craig, M.A., B.Sc., Frank Dixon, Arnold Eiloart, Ph.D., Thomas Ewan, B.Sc., Ph.D., Charles James Pemmeller Fuller, Walter Thomas Grise, William Harrington, James William Helps, Albert Howard, Ernest Haynes Jeffers, James Johnstone, Cass L. Kennicott, Laurence W. Mathieson, Joseph Edward Morrison, Harold Rostron, B.Sc., Thomas Francis Rutter, B.Sc., Charles Edward Sage, Arthur Philip Salt, Peter B. Scotland, Aitken Migget Simpson, Amrita Lal Sircar, L.M.S., Henry George Smith, Benjamin Bernard Turner, B.Sc.

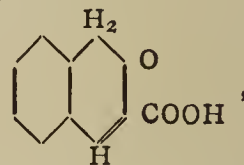
Of the following papers those marked * were read:—

*21. "The Origin of Colour. No. XI. The Yellow Colour of 2:3-Hydroxynaphthoic Acid." By HENRY E. ARMSTRONG.

Möhlau, in a recent most interesting note (*Ber.*, 1895, 3100), draws attention to the remarkable fact that 2:3-hydroxynaphthoic acid and a number of its derivatives are coloured (yellow) substances. On account of this peculiarity, he proposes to substitute for the conventional formula.



the isodynamic expression—



and seeks to explain the fact that the ethylic salt of the acid dissolves in alkali, yielding a yellow solution, by the assumption that a yellow sodium derivative is produced by the displacement of one of the two hydrogen atoms in position 1.

These new formulæ do not seem to harmonise with any conception which can at present be formed as to the inter-relationship of colour and structure, a subject to which the present writer has so often directed attention in communications to the Society (compare *Proc. Chem. Soc.*, 1890—93). It is not difficult, however, to account for the appearance of colour in such a case by an assumption similar to that already made use of by him in the case of certain terephthalic and other benzenoid compounds, as well as of certain quinoline derivatives (*Proc. Chem. Soc.*, 1892, 103; 1893, 13, 52, 55, 206; *Trans.*, 1892, 789).

Whatever the exact structure of naphthalene may be, it is presumably centric in form, and not ethenoid, although its great activity in comparison with that of benzene may be regarded as evidence of a strong tendency to change its form. If it be supposed that, owing to the strong tendency which oxygen exhibits in so many benzenoid compounds to assume the keto-form, 2:3-hydroxynaphthoic acid can pass from the hydroxy- to the isodynamic keto-form, and in so doing affect the structure of the cycloid itself, in the manner shown by the following symbols:—



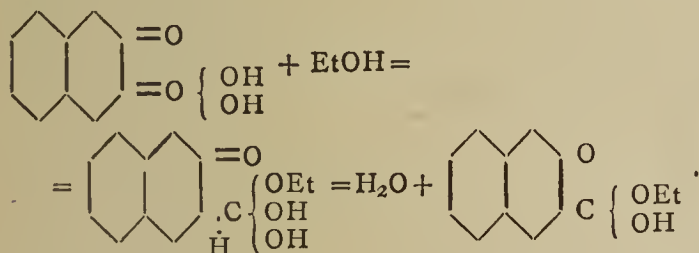
the yellow colour is accounted for without difficulty, as such a compound would be not only an orthoquinonoid derivative of naphthalene, but also an orthoquinonoid derivative of benzene. The "ethereal salt" of such an acid would contain a free hydroxyl group, and might therefore well be acid.

The behaviour of the acid with phenylhydrazine, to which Schöpf has just drawn attention (*Ber.*, 1896, 265), is without difficulty expressed by the formula here suggested.

*22. "Note on Etherification." By HENRY E. ARMSTRONG.

Möhlau, in the paper referred to in the foregoing note, calls attention to V. Meyer's observation that the 2:3-acid in question is converted into an ethylic salt more readily than is the isomeric α -hydroxynaphthoic acid, and regards this as strong evidence in favour of his view of the constitution of the acid.

An acid represented by a formula such as is suggested above would probably be particularly prone to combine with an alcohol, thus—



Attention is now drawn to this with the object of raising the question whether some such explanation may not apply to the remarkable generalisation at which V. Meyer has arrived in the case of diortho-substituted acids, and which he has sought to justify by introducing space considerations.

The formation of a salt is presumably preceded by that of a combination of acid and "alkaloid," from which water is then eliminated. Just as the acid-attracting power of the NH_2 radicle in aniline is affected by the introduction, say, of chlorine, so, in like manner, the "alkaloid" attracting power of the carboxyl group may be assumed to vary as radicles are introduced in its neighbourhood in place of hydrogen—more particularly in the case of benzenoid compounds.

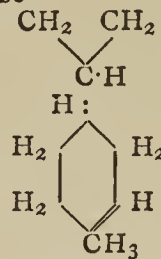
Apparently such effects are not sufficiently taken into account—the observations on the dimethylanilinesulphonic acids made in the writer's laboratory by Miss Evans (compare *Proc. Chem. Soc.*, 1895, 235), may be referred to as of considerable interest from this point of view, showing as they do that the mere introduction of two methyl groups into the NH_2 -group in place of the hydrogen altogether modifies the character of the compound, rendering it insensitive to the action of bromine in a most remarkable manner. It is intended to make experiments to ascertain if the introduction of different alkyls into the carboxyl group affect the behaviour of acids in any similar manner.

*23. "The Relation of Pinene to Citrene." By HENRY E. ARMSTRONG.

A. v. Baeyer in his recent (13th) note on orientation in the terpene series, shows in a most interesting manner that the genetic connection existing between pinene and citrene is far closer than has hitherto been supposed. It may, therefore, be desirable to briefly put on record an idea with reference to pinene which has long been in the writer's mind, and which has led him to regard the problem of its constitution from a point of view somewhat similar to that by which v. Baeyer appears to have been guided.

The fact that, under certain conditions, pinene behaves as a monethenoid compound, and yet under others readily gives derivatives, such as the citrene dihydrochlorides, led him, several years ago, to consider the possibility of

its being a trimethylene derivative, the simplest expression for which would be—



It is unnecessary to point out how such a compound would pass into a citrene-dihydrochloride such as may be derived from Tiemann's citrene formula, the formation of which from a dipentamethylene derivative such as pinene is represented to be by both Bredt and Tiemann is very difficult to understand—not to say eminently improbable.

The explanation of the formation of a compound having the properties of the hydrochloride obtained from pinene—artificial camphor—offers perhaps the greatest difficulty at present. This compound can scarcely be a direct derivative of pinene, and seems to be closely related to camphor—in fact, the writer has obtained a small quantity of camphoric acid by its oxidation with nitric acid. It appears not improbable that some more or less profound change attends its formation, and, with the aid of the formula given above, it would not be difficult to represent the production from the trimethylene radicle of a new penta- or methyl-tetramethylene ring attached to contiguous carbon atoms of the hexamethylene ring, and thus to arrive at a formula such as the writer long ago attributed to camphor.

That many of the derivatives obtained from camphor are the end-products of a series of analytic and synthetic changes there can be no doubt. It is impossible to explain the formation of substances so different as cymene, metacymene, ethyldimethylbenzene, carvacrol, and acetylorthoxylene in any other way. At one time we thought but of its relation to cymene; latterly the relation of camphor to trimethylsuccinic acid has monopolised attention: but it may well be that the latter, like the former, is an elusive support, and owes its formation to atomic redistribution.

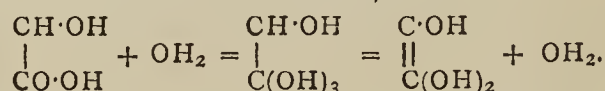
It may be pointed out that "artificial camphor," pinene nitrosochloride, and pinene dibromide differ in a remarkable and significant manner in optical properties, the first alone being optically active. It is to be remembered that the carbon atoms which are connected by an ethenoid linkage in pinene cannot be the origin of its optical activity, and, whatever its formula, it must be one containing at least one asymmetric carbon atom. But, this being the case, it is difficult to understand how the addition, either of bromine or of nitrosyl chloride, can give rise to optically inactive products capable of affording an inactive pinene; the occurrence of "racematisation" in such a case would seem to indicate that the region in which the asymmetric carbon is situated also becomes affected, although, apparently, but temporarily; *i.e.*, whatever be the change, it is subsequently reversed, even when pinene is converted into the nitrosochloride. If we cannot accept this conclusion, we must admit that the formulæ hitherto attributed to pinene are all unsatisfactory expressions to a far greater extent than we have ever supposed. The difficulty, it may be added, is greater in the case of such a formula as Tiemann's—as this contains two asymmetric carbons—than in the case of those proposed by v. Baeyer, or by the writer.

A similar argument is applicable in the case of camphor. If the argument of the following note be admitted, the production of an inactive campholide on reduction of camphoric anhydride (Haller, *Comptes Rendus*, 1896, 295) may, in fact, be regarded not only as a proof that the CO group undergoing reduction is connected with an hydrogenised asymmetric carbon atom, but also as evidence of the presence of but a single asymmetric carbon in camphor.

*24. "The Conditions involved in the Occurrence of Inversion in the case of Asymmetric (Optically Active) Compounds." By HENRY E. ARMSTRONG.

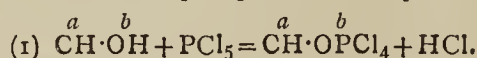
Having formed the opinion that the changes which attend the production of what are supposed to be pinene derivatives merit much closer attention, the writer has been led to carefully consider Walden's recent very remarkable observations on the formation from each of the two active malic acids by means of phosphorus pentachloride or bromide of an oppositely active chloro- or bromo-succinic acid, from each of which in turn a malic acid of its own order of activity may be obtained (*Ber.*, 1896, 133). It does not appear difficult to explain these results without any modification of our current theory, and attention is now called to considerations which, perhaps, may prove to be of importance in discussions of the behaviour, and of other questions relating to, asymmetric compounds.

When opheal inversion is effected by hydrolytic agents, in the case of an aldose, or of a ketose or acid, it is probable that, in the first instance, the keto-group becomes hydrated, and that either an "aldehydrol," $\text{CH}(\text{OH})_2$, or a "ketohydrol," $\text{C}(\text{OH})_2$, or an "acidhydrol," $\text{C}(\text{OH})_3$, is produced. When water is withdrawn from such compounds, if the water be formed from an OH-group of the hydrol complex and a hydrogen atom attached to the carbon contiguous to that of the hydrol complex, an ethenoid derivative will be formed, thus—

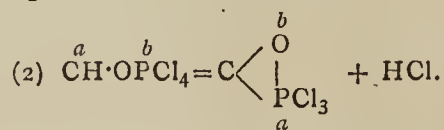


On hydration, according as hydration takes place at the one or the other junction of the ethenoid linkage, such a compound will afford one or the other of the two possible asymmetric forms, and if, as in the case of tartaric acid, the compound be symmetrical, it is to be expected that the two forms will be produced in equal proportions. But if an unsymmetrical compound be thus changed, such as a hexose or an acid like gluconic acid, it is to be expected that the severance will take place to a greater extent at one of the two junctions, and in some cases perhaps only at one. The striking results recently obtained by Lobry de Bruyn, and all E. Fischer's observations, are in accordance with this view, which, in fact, is the generally accepted one.

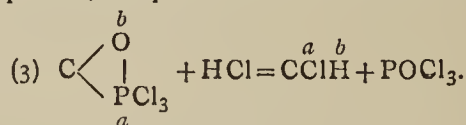
When malic acid is acted on by, say, phosphorus pentachloride, probably the first action to occur is one involving the formation of a chlorophosphonium compound, thus,—



The next stage in the change may be assumed to be one involving "internal condensation,"—



Supposing that this compound be then acted on by hydrogen chloride and resolved into chlorosuccinic acid and phosphorus oxychloride, if the attack became directed by the phosphorus, so that the chlorine took up the position of the phosphorus, complete inversion would be effected:—



It will be obvious that such an explanation may be of general application, especially in connection with the exclusive production, under natural conditions, of a single asymmetric form.

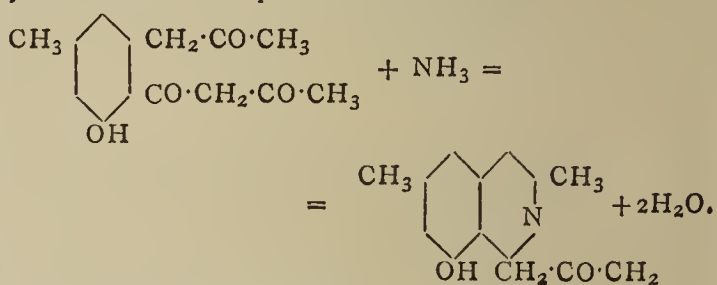
*25. "The Production of Naphthalene and of Isoquinoline Derivatives from Dehydracetic Acid." By J. NORMAN COLLIE, Ph.D., and N. T. M. WILSMORE, M.Sc.

It was shown by one of the authors (*Trans.*, lxiii., 329), that, under certain conditions, diacetylacetone condenses forming a yellow crystalline compound, apparently a benzene derivative, and that this further condenses easily, forming a second yellow compound, which was shown to be a derivative of naphthalene.

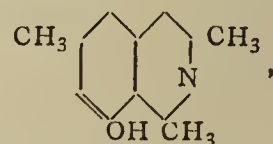
On the average, dehydracetic acid yields about a quarter of its weight of the first compound. A dioxime of the first yellow compound has been prepared in a nearly pure state. By distilling the diacetate of the second yellow compound with zinc dust, a naphthalene hydrocarbon, m. p. 75–78°, has been prepared. Its composition agrees well with that of a dimethylnaphthalene. On oxidation with dilute nitric acid it yields an acid, giving the fluorescein reaction. Analysis of the silver salt of this acid agrees with the composition $\text{C}_9\text{H}_6\text{O}_2\text{Ag}_2$; and the melting-point, 115–120°, coincides fairly well with that found for benzene 1 methyl 3, 4 dicarboxylic acid (*Ber.*, 1892, 2108). By the action of strong sulphuric acid on the second yellow compound (dimethylacetodinaphthol), a colourless substance results.

By the action of strong ammonia on the first yellow compound, a yellow basic substance ($\text{C}_{14}\text{H}_{15}\text{NO}_2$) is produced, soluble in water and in alcohol, forming intensely yellow solutions. The chloride and platinichloride were prepared and analysed. On heating with strong sulphuric acid, acetic acid is given off, and the sulphate of another base is left. This base has the composition $\text{C}_{12}\text{H}_{13}\text{NO}$. On oxidation it yielded an acid, which appeared to be a lutidine dicarboxylic acid, $\text{C}_9\text{H}_9\text{NO}_4$.

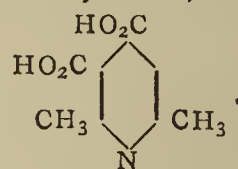
The authors consider it probable that these bases are derivatives of isoquinoline formed by condensation of the yellow benzene compound with ammonia.



The second base would be—



and the lutidine dicarboxylic acid,—



*26. "Note on a Difficulty encountered in the Determination of Nitrogen by the Absolute Method." By WYNDHAM R. DUNSTAN, F.R.S., and F. H. CARR.

The percentage of nitrogen in aconitine determined by the soda-lime process, using the base, or by the absolute method, using the hydrochloride, agrees well with that calculated from the formula $\text{C}_{33}\text{H}_{45}\text{NO}_{12}$, which is 2.1 per cent. A few years ago, Richards and Rogers (*Chemist and Druggist*, xxxviii., 242) stated that when the amount of "nitrogen" in aconitine is determined in the usual manner by the absolute method, it is found to correspond with nearly twice the percentage calculated from the formula given above, and they, therefore, proposed to alter the formula of aconitine to $\text{C}_{33}\text{H}_{43}\text{N}_2\text{O}_{12}$, in accordance with the results of their determinations. At that time the present writers were unable to look into the cause of these high results, but they were satisfied as to the accuracy of previous determinations (with the hydrochloride), showing

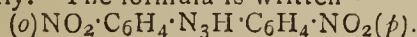
that the molecule of the alkaloid contains but one atom of nitrogen. Recently they have had occasion to determine the nitrogen in the base by the absolute method, the air being expelled from the combustion-tube by carbon dioxide, and the gas collected in an azotometer. They were surprised to find that over 4 per cent of gas was obtained instead of 2.1 per cent, the calculated quantity. The determination has since been repeated by four independent observers, every precaution being taken to ensure complete combustion by employing a long layer (about 60 c.m.) of red-hot copper oxide, and by conducting the burning slowly. The percentages obtained were 4.4, 5.3, 5.1, 3.8, 4.0, 4.1, 4.3. The highest percentages were obtained when the burning was conducted at about the usual rate, the lowest numbers by burning extremely slowly and maintaining the temperature as high as possible throughout the process. Similar results were obtained when the combustion was conducted in a vacuum, and the gas drawn off through a Sprengel pump in the manner suggested by Frankland and Armstrong. The hydrochloride of the alkaloid, however, when burned in either way gives a percentage only slightly higher than the calculated amount. Strychnine and some other typical nitrogenous organic compounds have been burnt in precisely the same manner as aconitine, but the percentages found were, as usual, only slightly higher than those calculated from the formula.

A quantity of this gas having been collected in different experiments which had given too high results, a complete analysis of it was made. Nitric oxide and carbon monoxide were absent. By exploding with excess of oxygen, measuring the contraction, and absorbing the carbon dioxide, methane was proved to be present. Estimating the methane in the mixed gas, and deducting it from the total volume taken, the nitrogen amounted to almost exactly 2.1 per cent, corresponding with that calculated from the formula $C_{33}H_{45}NO_{12}$.

Experiments made with artificially prepared mixtures have shown that when largely diluted with nitrogen, methane is burnt very slowly and with difficulty by red-hot copper oxide. In conducting the process in the usual manner the influence of the carbon dioxide used to expel the air from the tube no doubt greatly aggravates the difficulty. Aconitine seems to be exceptional in giving rise to so much methane during combustion. Possibly the difficulty might be overcome by mixing the alkaloid, not merely with finely powdered copper oxide, but also with a more powerful oxidising agent, as, for example, lead chromate. Neither aconitine hydrochloride, benz-aconine, nor aconine hydrochloride present this anomaly, and it has been observed that if aconitine is introduced into the tube along with a little cuprous chloride, the percentage of gas obtained corresponds very nearly with the calculated quantity.

27. "Mixed Diazoamides containing an Orthonitro-Group." By RAPHAEL MELDOLA, F.R.S., and FREDERICK WILLIAM STREATFEILD, F.I.C.

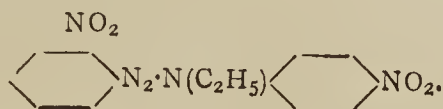
Orthodinitrodiazoamidobenzene, which was prepared and described by the authors in their last communication on this subject (*Trans.*, 1894, 52), does not appear to be capable of ethylation by the usual methods (*loc. cit.*). As this is the first exception that has yet been found to the general method of alkylating the diazoamides introduced by the authors in 1886 (*Trans.*, 1886, 624), it became of special interest to ascertain whether the usual triplet of isomerides could be prepared when an orthonitro-group was present on one side of the chain of nitrogen atoms. The mixed diazoamide from ortho- and para-nitraniline was prepared by both methods of combination in the usual way, and the product found to be identical irrespective of the order of diazotising. So far the production of the compound is quite normal. After crystallisation from alcohol it consists of golden yellow scales melting with decomposition at 192–193° when the temperature is raised rapidly. The formula is written—



The compound is decomposed by excess of strong hydrochloric acid at ordinary temperatures into the usual mixture of four products, viz., ortho- and para-nitraniline and the corresponding diazo-chlorides. It has the acid characters common to all the dinitrodiazoamides, dissolving in alkaline solutions with a reddish colour, and being precipitated unchanged by acids. By the action of ethyl iodide on the potassium salt in alcoholic solution the ethyl derivative is obtained in the usual way. The latter consists of orange needles melting at 177–179°.

A special attempt was made in this case to separate the mixed diazoamide into isomerides by fractional ethylation, but the result was negative, the product being simply a mixture of unethylated compound (m. p. 192–193°) and the ethyl derivative (m. p. 177–178°). Under all circumstances, the ethylation of this diazoamide is incomplete, a certain amount of unchanged substance being left in the mother liquor, even when potassium hydroxide and ethyl iodide are used in excess.

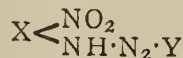
The behaviour of the ethyl derivative towards hydrochloric acid is quite exceptional, and the products of its decomposition are ethyl-*p*-nitraniline and orthonitrodiazo-benzene chloride. This is the first instance which has come under our observation in which an alkyl-diazoamide from the direct alkylation of a mixed diazoamide has given only two instead of four products on decomposition by acid. This ethyl derivative is also remarkable for its stability towards hydrochloric acid, as it had to be kept at a temperature of about 80–90° for some hours in presence of a large excess of acid before decomposition was complete. Not a trace of nitrogen was evolved during the decomposition. The products were identified by filtering the cold acid solution into an alkaline solution of β -naphthol (*Trans.*, 1887, 438) and collecting the bright red precipitate which at once formed. The latter, after washing with water, was extracted with hydrochloric acid, which removed ethyl-*p*-nitraniline; melting-point of nitrosamine 119–120° (*Trans.*, 1886, 631). The red residue proved to be orthonitrobenzeneazo- β -naphthol, m. p. 210° (Meldola and Hughes, *Trans.*, 1891, 374). These results indicate for the ethyl derivative the definite formula—



This view was confirmed by combining diazotised orthonitraniline with ethyl-*p*-nitraniline when the same compound (m. p. 177–179°) was obtained, and not an isomeride.

The explanation of the exceptional behaviour of this ethyl derivative is bound up with the general question of the "protecting influence" of a nitro-group in the ortho-position, as shown more especially by the recent researches in Victor Meyer's laboratory, which bring out very clearly the influence of ortho-substituents in preventing alkylation of the carboxyl group.

The System—



is incapable of being alkylated when NO_2 and NH are in the ortho-position. An attempt to prepare the isomeride by the action of diazotised paranitraniline on ethyl-*o*-nitraniline brought out still more forcibly the influence of the orthonitro-group. Combination could not be effected under any of the conditions which so readily furnish the other alkyl-diazoamides; paranitrodiazo-benzene chloride does not appear to have any action on ethyl-*o*-nitraniline.

It may be of interest to state in conclusion that these results are of great importance as establishing the fixity of the alkyl group when once introduced into a diazoamide. If this group were at all "labile," it might have been expected that by the action of diazotised paranitraniline on ethyl-*o*-nitraniline the same compound would have been obtained as by the action of diazotised

orthonitraniline on ethyl-*p*-nitraniline. In the former case, as we have proved, the compounds remain for days in contact without combining. The difficulty which we have experienced in preparing ethyl-*o*-nitraniline is also due to this same influence of the orthonitro-group. Since orthodinitrodiazoamidobenzene cannot be ethylated, we were unable to prepare it by the decomposition of this compound. Attempts to ethylate orthonitraniline directly gave unsatisfactory results, as also did the published methods (*Beilstein*, vol. ii., 332). The simplest method, according to our experience, is to heat orthonitrophenol ether (ethyl) with alcoholic ethylamine in a sealed tube for twelve hours at 150°.

28. "*Allyl p-Dinitrodiazoamidobenzene: a Study of the Relations between Melting-point and Constitution.*" By RAPHAEL MELDOLA, F.R.S., and FREDERICK WILLIAM STREATFIELD, F.I.C.

As the introduction of alkyls into diazoamides always lowers the melting-point, the lowering being greater the greater the weight of the homologous radicles introduced, the above compound was prepared with a view to ascertaining whether the same rule holds good for unsaturated radicles. It was found that paradinitrodiazoamidobenzene could be quite readily converted into an alkyl derivative by the action of potassium hydroxide and allyl iodide in the usual way. The pure compound forms small yellow needles, m. p. 164—165°.

0.0826 gave 15.1 c.c. moist nitrogen at 14.5° and 759.4 m.m. = 21.42 N. $(p)\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{N}(\text{C}_3\text{H}_5)\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2(p)$ requires N = 21.40 per cent.

The melting-point of the original compound is about 236° (if the temperature is raised very rapidly), of the methyl derivative 219°, of the ethyl derivative 191—192°, and of the benzyl derivative 190° (*Trans.*, 1887, 112). Taking the upper limit of temperature at which the original compound decomposes (236°) the depression produced by methyl is 17°, ethyl 44°, benzyl 46°, and allyl 71°. It thus appears that the unsaturated radicle lowers the melting-point to the same extent (27°) as the difference between the methyl and ethyl derivatives, and so far allyl may be said to exert a normal influence. In other words, the difference between the allyl and ethyl derivative is the same as between the ethyl and methyl derivative. Since benzyl produces practically the same lowering as ethyl, it would further appear that the nature of the group in direct combination with the nitrogen atom is of paramount influence, and that any other radicles associated with this group, such as C_6H_5 in $\text{CH}_2\cdot\text{C}_6\text{H}_5$, are of subsidiary influence. The actual weight of the introduced radicle is thus of small importance as compared with its constitution.

NOTICES OF BOOKS.

Petroleum: a Treatise on the Geographical Distribution and Geological Occurrence of Petroleum and Natural Gas; the Physical and Chemical Properties, Production, and Refining of Petroleum and Ozokerite; the Characters and Uses, Testing, Transport, and Storage of Petroleum Products, and the Legislative Enactments relating thereto; together with a Description of the Shale Oil and Allied Industries. By BOVERTON REDWOOD, F.R.S., F.I.C., Assoc. Inst. C.E., V.-P. Soc. Chem. Industry, F.C.S., F.G.S., F.R.G.S., &c. Assisted by G. T. HOLLOWAY, Assoc. R.C.S., F.I.C.; and other Contributors. In Two Volumes, with numerous Maps, Plates, and Illustrations in the Text. Vol. I. London: Charles Griffin and Co. (Ltd.). 1896. 8vo., Pp. 900.

THE gigantic importance, in modern industry and commerce, of petroleum and its products, fully justifies the appearance of a work of the encyclopædic character of

the two volumes before us, and their authorship could not have devolved upon a more qualified expert than Mr. Boverton Redwood. The subject is here viewed under its multiform aspects, chemical, geological, engineering, and sanitary. The author has had the opportunity of visiting and reporting on the petroleum fields and refineries of the United States and of Russia, and has, in addition, collated the researches of others.

An inspection of the accompanying map of the world will convince us of the very extensive distribution of this useful mineral. Petroleum wells seem most plentifully distributed in the Eastern hemisphere, in a belt extending from the Malay Islands, through India, Persia, the shores of the Caspian, Southern and Central Europe as far as Spain. In Siberia and Northern Europe petroleum has been as yet rarely and sparingly discovered. With the exception of Morocco and Egypt, and one locality near Cape Coast Castle, Africa is devoid of this inestimable product. Australia is equally poor.

In the Western Hemisphere we encounter petroleum in a belt stretching from Alaska in a south-easterly direction to the Alleghanies, where it is most splendidly developed. It is then met with more sporadically in Mexico, the West Indies, Colombia, Peru, down to near the mouth of La Plata.

We have no right to say that petroleum may not exist to an important extent in the countries where it has not yet been obtained, but so far as research has gone it seems to affect the volcanic regions of the world. Hence its scanty occurrence in Africa, Australia, and Brazil,—its remarkable association with salt and with mud volcanoes, as in Arrakan.

The origin of petroleum has given rise to much speculation and research, though it cannot be said that any one theory has obtained general acceptance. The view of an inorganic origin, supported by such eminent authorities as Mendeleeff, and Berthelot, Bischoff, and others, is still doubtful. The theory of its origin from organic remains, animal or vegetable, is upheld by Sterry Hunt, Newberry, Packham, Höfer, Orton, and others, and appears to be in the ascendant. Our author, however, judiciously concludes that no one theory seems to account for all the phenomena of the production of petroleum in every case.

A large portion of the second volume is devoted to the legislation adopted in different countries touching the importation and storage of petroleum. It is to be noted that the original British standard, 100° F., as fixed in 1862, has been withdrawn, and our present standard, established in 1879, is 73° F. This standard is generally considered as perilously low, but any administration which should propose an amended standard would incur the bitter hostility of all persons interested in the trade. In the State of Illinois the limit fixed is 150°, and we learn that inferior oils are with all diligence shipped off to Britain.

Mr. Boverton Redwood has made in these volumes a splendid contribution to our technical literature.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxii., No. 3.

Mercury in Asturias.—A. Dory.—Asturias produced, in 1883, 4000 bottles of mercury of 34.503 kilos. each.

Deposit of Cinnabar at Gratwein-Eisbach, in Styria. — Jules François. — The cinnabar of Gratwein yields 5.72 per cent of mercury for the richer kind of ore, and 4.12 per cent for the poorer kind.

Researches placed at the Service of Medicine and Surgery by Electrical Science.—Prof. Eric Gérard.—The effects of this potent agent may assume a mechanical form, as in the case of neuro-muscular contractions, and the transfer of liquids and dissolved salt with the current. The effects taking a chemical form in electrolysis are utilised for decomposing tissues or causing reagents to pass through them. Lastly, we have observed thermic results. But electricity demands to be managed with discernment. I wish that the faculties of medicine would require one of their members to teach the principles of electro-therapathy.

The British Imperial Exhibition at Montreal.—This Exhibition will open on May 24th next, and will have sixteen sections, — *i. e.*, architecture and forests, means of transport, general industries, food industries, sea and river fisheries, hygiene, machinery, lighting, industrial arts, heating, geology, furniture, protection to life, horticulture, insurances, various.

MISCELLANEOUS.

The Madrid Aërolite.—In connection with the explosion of an aërolite, which occurred in the atmosphere at Madrid, on the 10th of February last, at 9.30 in the morning, during bright sunshine, and throwing the whole city into a state of consternation, the Queen Regent of Spain has caused the following letter to be addressed to Dr. Phipson, of Putney, author of a work on these curious phenomena:—"Madrid, 20 February, 1896. Sir,—Having had the honour of placing in the hands of Her Majesty the Queen Regent the copy you have kindly sent her of your work, 'Meteors, Aërolites, and Falling Stars,' my august Sovereign has deigned to command me to thank you in her Royal name for sending her so interesting a work. Accept, Sir, the expression of my distinguished consideration.—(Signed) Count MORPHY."

The Wiesbaden Chemical Laboratory.—The Chemical Laboratory of Professor Dr. R. Fresenius has been attended by fifty-five Students during the Winter Session of 1895–96. Thirty-nine of these were German, six were English, and two Belgian, and the remaining eight came respectively from the United States, Norway, Sweden, Holland, Russia, Italy, Spain, and Australia. There were three assistant demonstrators in the several teaching departments, and twenty-three assistants in the Versuchsstationen (private laboratories). The Royal Prussian Minister of Education has given the certificate of qualification as food analyst to Prof. Dr. R. Fresenius, Prof. Dr. H. Fresenius, Dr. W. Fresenius, and Dr. E. Hintz. In addition to these Professors of the Establishment there are the following:—Dr. G. Frank (Bacteriology and Hygiene), Dr. W. Leng (Microscopy), Dr. L. Grünhut (Technology), and Mr. T. Brahm (Technical Drawing). The next Summer Term begins on the 24th of April. Throughout the Winter Session, besides various scientific researches, a great number of analyses have been undertaken in the different departments of the Laboratory for manufacturers of all kinds, in judicial cases, and in many branches of trade, mining, agriculture, and hygiene.

MEETINGS FOR THE WEEK.

TUESDAY, 17th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.
— Institute of Civil Engineers, 8.
— Photographic, 8.
— Pathological, 8.30.
WEDNESDAY, 18th.—Society of Arts, 8. "The Bahamas Sisal Industry," by Dr. D. Morris.
— Meteorological, 7.30.
— Microscopical, 8.

THURSDAY, 19th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "Masters of Modern Thought—III. Goethe," by The Rev. W. Barry, D.D.
— Society of Arts, 8. "The Great Landslip at Gohna, in Gu-hwal," by J. H. Glass, C.I.E.
— Chemical, 8. "The Constitution of a New Organic Acid," by H. J. H. Fenton, M.A. "The Volume and Optical Relationships of the Monoclinic Series of Double Sulphates, $R_2M(SO_4)_2 \cdot 6H_2O$," by A. E. Tutton.
FRIDAY, 20th.—Royal Institution, 9. "Immunisation against Serpents' Venom and the Treatment of Snake-Bite with Antivenene," by Prof. T. R. Fraser, F.R.S.
— Quekett Club, 8.
SATURDAY, 21st.—Royal Institution, 3. "Light," by Lord Rayleigh, F.R.S., &c.

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The Rivers Committee are prepared to receive Applications for the post of Chemist in the City Surveyor's Department. Applicants must afford proof of competent knowledge of Chemistry and Bacteriology. Salary £200 per annum. The whole of the time must be devoted to the work of the Corporation. Particulars of duties may be obtained at the City Surveyor's Office, Town Hall, Manchester.—Applications, accompanied by copies of three recent testimonials, to be addressed to the Chairman of the Rivers Committee, and delivered at the above office at or before noon on the 21st March instant.

WM. HENRY TALBOT, Town Clerk.

9th March, 1896.

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Candidates in Technology not attending any registered Class should apply at once to the Secretary of the nearest local centre.

Applications from individual Candidates for Examination at the Central Technical College should be made not later than April 18th, addressed, 'City Guilds Institute, EXAMINATIONS DEPARTMENT, Exhibition Road, S.W.,' and should be accompanied by a Postal Order for the amount of the fee.

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E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic) Prof. H. FRESENIUS, Ph.D.
Experimental Physics W. FRESENIUS, Ph.D.
Stoichiometry E. HINTZ, Ph.D.
Organic Chemistry L. GRUNHUT, Ph.D.
Chemical Technology W. LENZ, Ph.D.
Microscopy, with exercises in Micro-
scopic work
Chemistry and Analysis of Foods .. { Prof. H. FRESENIUS, Ph.D.
W. FRESENIUS, Ph.D., and
E. HINTZ, Ph.D.
Hygiene Dr. med. G. FRANK.
Practical exercises in Bacteriology ..
Technical Drawing, with exercises .. J. BRAHM.

The next Session commences on the 24th of April. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to the undersigned.

Prof. R. FRESENIUS, Ph.D.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1895.

ON THE PASSAGE OF THE RÖNTGEN RAYS THROUGH LIQUIDS.

By MM. BLEUNARD and LABESSE.

IN studying the influence which liquids may have on the passage of the Röntgen rays, it was necessary for us first to avoid the errors which might result from the transit of the rays through the vessel in which liquids have to be placed.

Glass is one of the substances which offer the greatest resistance to the passage of the Röntgen rays. On the other hand, vessels of wood or cardboard, covered with a layer of fatty matter, still oppose, in a certain degree, the passage of the rays. We have found that black paper, coated with suet, is, on the contrary, absolutely permeable. The sensitive plates wrapped up in ordinary black paper, upon which are arranged squares of paper coated with tallow, are acted upon by the rays with the utmost ease, without any trace indicating upon the plate the arrangement which has been given to the little trough of greased paper.

If we expose to the Röntgen rays a sensitive plate previously wrapped in black paper, upon which are placed equal depths of liquid in small paper troughs coated with tallow, the white spots obtained upon the sensitive paper must be exclusively due to the liquids forming the screens.

We have hitherto made only summary experiments, but some of the results already obtained present, we believe, a certain interest.

Water is easily traversed by the rays.

Solutions of potassium bromide, antimony chloride, potassium bichromate, offer a very considerable resistance to the passage of the Röntgen rays, whilst solutions of sodium biborate and potassium permanganate are more easily traversed.

Colours seem to have no influence on the passage of the rays. Water coloured with various aniline colours offers no resistance.

Our intention is to pursue these researches.—*Comptes Rendus*, cxxii., p. 527.

OBSERVATIONS ON THE SUBJECT OF PHOTOGRAPHY THROUGH OPAQUE SUBSTANCES.

By A. D'ARSONVAL.

THE *savants* who have attempted to repeat the experiments of Le Bon are divided into two groups; some have obtained positive results, *e.g.*, Armagnac (of Bordeaux), Murat (of Havre), Braun (of Paris), &c.; others, like the Lumières, Londe, Monod, &c., have obtained no images.

I have myself repeated these experiments, and I think I have succeeded in finding the cause of the discrepancy among observers equally conscientious and skilful. Both are right: all depends on the experimental conditions. On operating like MM. Lumière, *i.e.*, on exposing to the solar rays a sensitive plate protected by a metal screen, I obtained no impression on the plate, even when the screen consists of a very slender plate of aluminium. The metal is therefore not traversed by the solar radiations, which seems to argue against the results obtained by Le Bon.

It is no longer the same if we interpose between the metallic plate and the solar rays a thick plate of glass,

like those which we find in the frames used for taking positives. Under such circumstances I have found in sufficient time, like M. Le Bon, a very feeble impression on the sensitive plate. If we place upon the metallic plate a piece of uranium glass, the impression on the sensitive plate is obtained more quickly. All glasses are not equally good. Those which give the best results are such as have a greenish yellow fluorescence if illuminated in the dark by the electric spark. I have further observed that it is the same with the phials yielding Röntgen's rays. We may substitute for the Crookes phial an incandescence lamp which is rendered fluorescent by connecting the filament with one of the poles of a coil of great frequency.

All the glow lamps which give a yellowish green fluorescence may be very well substituted for the Crookes phial; those, on the contrary, whose fluorescence is violet or bluish, give scarcely anything. I have also obtained a good result on using a single Geissler tube surrounded with a solution of fluoresceine.

In a word, it results from the above experiments that all the substances which emit fluorescent radiations of a yellowish green colour can act upon a photographic plate through opaque bodies.

The above contradictory results are very easily explained if we keep in mind the facts pointed out by Charles Henry, Nievenglowski, and especially by our colleague Henri Becquerel in the recent sessions. Fluorescent substances emit radiations having the properties of the X rays, in conformity with the hypothesis of our colleague Poincaré.

From all these facts it results that the rôle of the cathodic rays in Prof. Röntgen's experiments is limited to exciting the fluorescence of the special glass of which the Crookes phials are made.—*Comptes Rendus*, cxxii., p. 500.

ON DARK LIGHT: A REPLY TO CERTAIN CRITICISMS.

By GUSTAVE LE BON.

THE present paper is intended as a reply to the criticisms of MM. Lumière, who deny the existence of dark light; and to those of Zenger, who denies at once the dark light and the rays of Röntgen.

In reply to the critiques of MM. Lumière I point out that, even if we admit all their hypotheses, we should still find ourselves in presence of dark light. Light which is able, after being reflected at 93° three times successively, to pass between plates of glass and of metal, protected laterally by being fitted into a deep groove and compressed together by a weight of several kilos., will be totally invisible to the eye,—that is to say, precisely what I have called *dark light*.

We prove that it is invisible to the eye by placing ourselves in the conditions of our experiments. We form a pile of proofs, furnished behind and at their edges with black paper, and all our proofs are enclosed in such; we place then between them plates of metal, and submit the whole to a moderate pressure. If we view directly a luminous source along the edges of the system (even taking care to remain in darkness for a long time), we perceive absolutely no thread of light, although the source of illumination may be viewed directly without any of the successive radiations of which I have spoken.

When light penetrates into a case by any chink, the operator is at once made aware, by lines and veils, of a quite characteristic aspect. To obtain an image, even though very bad, the light must be admitted intentionally; but then the images produced are quite different from those obtained with dark light, as is proved by the specimens exhibited to the Academy.

The fact that MM. Lumière have obtained no images on pasting bands of black paper over all the edges of the

metallic plates is nothing surprising. According to the recognised laws of the distribution of static electricity, in conductive bodies the electricity does not traverse them, but is propagated by following their surface. I have supposed from some experiments that dark light is propagated in this manner. Whether it penetrates the plates or follows their outlines the result is the same. The slips of paper do not, doubtless, arrest the passage of the electricity, but since dark light, as I have indicated, is not entirely identifiable with electricity, it is quite admissible that the paper may act as an insulating body.

Various experimentalists have succeeded in obtaining results identical with mine. I mention among such M. Gaston Braun, a pupil of Prof. Eder, of Vienna, a son of the well-known Parisian photographer. As he has explained in a treatise recently published, he has adopted my arrangements, and has thus obtained reproductions of medals, of pieces of glass on which there had been traced designs, fishes, &c. He rightly remarks that the temperatures of the luminous source play a certain part.

I wrote to M. Braun to enquire the means of control which he had employed, especially for the reproduction of the medals. This is the substance of his reply:—No light stored up, since on performing the experiment in darkness after several hours no images were obtained. No lateral light through any fissure, since two plates were always side by side in the same frame, and the plate serving as a check never presented any veil. The plate of copper had exactly the dimensions of the frame, and was introduced with difficulty. No influence of the pressure of medals, since the same results were obtained on inverting a sensitive plate, *i.e.*, lacing the medals on the side of the glass.

As for the observations of Zenger relating to the non-existence of the X rays and of the dark light, they are perhaps better founded than the foregoing. His criticism is directed only to the interpretation of the results obtained. I see no impossibility in admitting that we have hereto do with "phenomena of electric induction producing phosphorescence in the gelatin, and at the same time an electric discharge in the gelatin." It is very possible that the dark light does not act directly upon the sensitive plate, and is limited to rendering fluorescent the objects placed behind the metallic plates. We know that the experiments of Charles Henry seem to verify the hypothesis of M. Poincaré that fluorescent substances emit X rays. Thus would be explained M. Murat's reproduction of the subcutaneous regions of a ray behind a plate of metal. This experiment may be repeated on separating the sensitive layer from the animal by a slender film of transparent celluloid, to avoid chemical actions. The fluorescence becomes even visible to the eye in certain cases not yet determined. It would explain how we may with some animals obtain analogous results in darkness, as I have shown in my former paper.

But what results clearly from the above, and especially from the discrepancy of the results obtained by different experimentalists, is that all the conditions of the transit of light through opaque bodies are not yet determined. I hope soon to succeed in rendering these experiments much easier to repeat.—*Comptes Rendus*, cxxii., p. 522.

DETERMINATION OF ARSENIC.

By ARMAND GAUTIER.

In the *Comptes Rendus*, vol. cxxii., p. 390, appears a paper by MM. Engel and Bernard on a "Rapid Process for the Determination of Arsenic," in which, whilst admitting the accuracy of the process for the same purpose which I published in 1875 (*Bull. de la Soc. Chimique* and *Annales de Chimie et de Physique*, 5th Series, vol. viii., p. 384), they think their method preferable in any case on account of its rapidity.

If I admit that the interesting procedure of MM. Engel

and Bernard has this advantage (which I do not think) I will point out that the method which I have indicated alone permits us, by weighing the arsenical ring obtained, with the precautions laid down, to determine exactly minimal quantities of this element, even below 1 m.grm.

As a proof I quote merely some figures which I have obtained:—

Quantities of arsenic introduced into the Marsh apparatus.	Weight of the arsenical ring obtained.
0.0038	0.0037
0.0038	0.0037
0.0019	0.0018
0.00188	0.0018

The numbers agree almost as well when it is required to extract and determine minute quantities of arsenic mixed with animal matter.

Such quantities, we think, could scarcely be determined by the method of the authors quoted.

Now, the exact determination of the slightest traces of this element is the object indispensable to be obtained in industry, when it is requisite, *e.g.*, to estimate a metallurgical process, or the value of a metal in which the slightest traces of arsenic often modify all its physical properties, its colour, its hardness, its tenacity, &c. The volatilisation of arsenic and antimony in the gaseous state alone permits us to determine and separate exactly the minutest quantities of these substances in ores, metals, and alloys where they may exist merely in very minute proportions.

This method has been employed by Prof. van 't Hoff in his researches on apparent exceptions to the law of Raoult when it is required to study mixtures of antimony and tin.

I must further remark that the method which I have published has the advantage of allowing arsenic and antimony, after being separated from the other metals, to be each determined in succession after the entire ring has been weighed.

I will, lastly, remark that this method alone enables us to determine arsenic as well in its mineral or organic combinations as when it exists in a latent state and in minimal quantities in the viscera of animals which have absorbed it during life.—*Comptes Rendus*, cxxii., p. 426.

EXTENSION OF NESSLER'S REACTION. DETECTION OF MERCURY AND IODIDES.

By G. DENIGÈS.

MERCURIAMMONIUM iodide-mercury oxide, which is formed by Nessler's reaction for the detection of ammonia, is readily obtained if we bring together a mercuric salt, ammonia, a caustic alkali, and potassium iodide, on condition that the salt last mentioned is not in excess, which would prevent the separation of the characteristic precipitate. For the production of this precipitate, the joint presence of the four substances just mentioned is necessary. If, in preparing the reagent, one of the four substances is omitted, the mixture can serve for the detection of the fourth substance, provided that other substances do not form a similar precipitate with the reagent. Experiments which I have made in this direction showed that the caustic alkali alone need be present in quantity, whilst mere traces of the other two are only needful for the detection of the fourth, by forming the mercuriammonium iodide mercuric oxide. It is here shown in what manner the Nessler reaction can serve for the detection of mercury and of iodides.

A.—Detection of Mercury.

1. *Simple Solutions of a Mercuric Salt.*—If it is desired to produce the precipitate in question with a mercuric salt, we put into a test-glass 2 c.c. of a 1 per cent solution

of mercuric chloride, add 1 c.c. of ammonia, and cause the precipitate thus produced to disappear by a suitable addition of potassium iodide. In general, 10 drops of a 20 per cent solution will suffice. In the detection of mercury by this method two cases are possible:—(a) The solution contains more than 0.5 grm. of mercury per litre, or (b) the solution is very dilute. In the former case the reaction is carried out as just indicated, with the precaution that the solution of iodide is added drop by drop in such a quantity as just suffices for re-dissolving the precipitate thrown down by the ammonia, or until a colouration just appears, when the lye is at once added and shaken up. In the second case we take 10 to 20 c.c. of the solution in question, add 1 c.c. ammonia, and the quantity of iodine solution just sufficient to re-dissolve the precipitate. If the mercuric solution contains only 1 to 2 centigram. per litre, one drop of the iodide solution is sufficient.

2. *Mercurial Compounds in general.*—If the substance is a liquid, we take 2 c.c.; if solid, we put a few centigrams. into a test-glass, add, in either case, 1 c.c. hydrochloric acid and 0.5 nitric acid, and boil the mixture until only a few drops remain in the test-tube. The residue is taken up in 5 c.c. of water, filtered (if needful), and to the solution thus obtained there are added 2 c.c. ammonia, with 2 to 10 drops of a 20 per cent solution of potassium iodide, according to the quantity of the mercury present, and shake up. The liquid either remains clear, in which case the reaction ensues on the addition of caustic alkali, or there appears a white or coloured precipitate. If the precipitate is white, the reaction is not interfered with, and addition of caustic lye is sufficient to bring up the characteristic reaction. If the precipitate is coloured it is filtered off, and the filtrate is mixed with caustic lye. A colour may appear on the addition of potassium iodide, e.g., in presence of copper. In this case we dilute strongly, so that the colour appears less intense, and then add the caustic lye.

If carried out in this manner, the Nessler reaction may serve for the detection of the smallest quantities of mercury.

B.—Detection of Iodides.

If the substance under examination contains metals which are precipitated by the reagent, we use the filtrate from the ammonium sulphide precipitate. We filter, acidulate with hydrochloric acid, boil until the hydrogen sulphide is expelled, and supersaturate with ammonia. We add to the liquid a little caustic lye and a few drops of mercuric chloride, and shake up. If there appears a precipitate of a more or less deep red colour we may infer the presence of iodine. In the absence of iodine, the precipitate is white or slightly yellowish. We can prepare fresh for each time of using a mixture of 1 c.c. ammonia, $\frac{1}{2}$ c.c. soda-lye, and a few drops of solution of sublimate. If this mixture, which is yellowish, is brought in contact with the liquid obtained above, there appears, in presence of iodine, the characteristic precipitate of mercuric ammonium-iodide mercuric oxide. The reaction is very sensitive, and is applicable also for insoluble iodides.—*Chemiker Zeitung.*

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 126.)

CHAPTER VII.

CHEMICAL RESEARCHES ON CARBONATE, NITRATE, AND CHLORIDE OF STRONTIUM.

Barium, calcium, and strontium are closely associated both in the form of carbonate and of sulphate. Sodium is an accidental impurity, as are also the silicon, iron, and

manganese met with in native sulphates and carbonates of strontium. After a few preliminary experiments, I made in the following way some carbonate of strontium free from foreign bodies, which I then used for the spectroscopic study of strontium, as well as for making nitrate and chloride of this metal.

I took as raw material some chloride of strontium that I had previously purified from iron and manganese, by means of a solution of sulphide of strontium, and which had then been crystallised five times in succession, removing the mother-liquor each time, but which still contained barium, calcium, sodium, and silica.

The crystallised chloride was moistened, in a covered platinum retort, with a solution of pure chloride of ammonium, dried, and then heated till the greater part of the sal ammoniac was volatilised. The residue was dissolved in cold water, and the solution filtered to separate the now insoluble silica. The clear liquid was evaporated until it became solid, and the residue moistened afresh with a saturated solution of chloride of ammonium. It was dried at a low temperature, and the residue was once more heated till it freely gave off vapours of sal ammoniac. The chloride was re-dissolved in cold water, and the solution, though apparently clear, was again filtered. Finally, it was treated a third time with sal ammoniac, so as to make sure of having eliminated all the silica.

The solution of chloride after this third treatment was, after being passed through a purified filter-paper, added to five times its own volume of pure water, and poured into water containing 5 per cent of pure sulphuric acid. The sulphates of barium, calcium, and strontium, formed in a very dilute liquid, were flocculent. After six hours rest in a platinum vessel, the clear supernatant liquid was poured off and replaced by pure water, and the washing was continued until the decanted water no longer turned blue litmus-paper red.

The sulphates in the platinum vessel were then put to digest, cold, for sixteen hours, in an excess of a solution of sesqui-carbonate of ammonium, the mixture being stirred up from time to time; the insoluble mass was then washed and re-washed by decantation until the decanted water had no effect on red litmus-paper.

According to accepted theories, all the barium in the chloride of strontium used should be in the insoluble mass in the form of sulphate, whilst the sulphates of strontium and calcium should be converted into carbonates. To verify this I took about one-tenth of the whole, and, having put it into water, I added hydrochloric acid, drop by drop, taking care not to destroy all the carbonate mixed with the sulphate of barium. The chloride solution was clouded, and did not become clear on passing through a filter-paper. I had to leave it to settle, and this took a long time. After settling, the liquid which had deposited the carbonate dissolved by carbonic acid was filtered, and poured again into water containing sulphuric acid. The resulting sulphate, having been carefully washed by decantation, was treated cold with an excess of a solution of sesqui-carbonate of ammonium. After twelve hours action the mother-liquor, though clouded, was poured off, and the washing was continued until the decanted water, which was always slightly clouded, was entirely neutral to red litmus-paper. I then put the carbonate into water, and gradually added pure nitric acid, until nearly all the solids were dissolved. The nitrate solution, clouded by the carbonate in suspension, was left to settle, and the liquid was then decanted and filtered. I then acted on the remaining carbonate with a very dilute solution of nitric acid, and it was dissolved, forming a clear liquid.

Thus the barium was entirely in the form of sulphate in the residue left after reacting on a mixture of sulphates of barium, calcium, and strontium, when cold, by bicarbonate of ammonium. By taking care not to destroy all the carbonate in the mixture, one is certain not to dissolve the sulphate of barium.

Having ascertained this fact I converted, in the cold,

the bulk of the carbonates of strontium and calcium left in the platinum vessel into nitrates, taking care to leave at least one-tenth of the carbonates. The solution was very cloudy, and was not cleared by passing through a filter-paper. It was therefore left to settle and then filtered; this was a very slow process. I added to the clear liquid the solution of nitrate of strontium made before, and evaporated the whole to dryness in a covered platinum retort.

The nitrate when dried was in small crystals. I treated it with absolute alcohol, first cold, then at boiling-point. I continued the treatment until the nitrate of calcium was dissolved. I then put the residue into pure water; the solution not being clear, was filtered. It left a very slight white precipitate, consisting entirely of a mixture of carbonate of strontium and calcium, which was put to one side. The solution was again evaporated to dryness, and the nitrate, as a crystalline powder, was treated with absolute alcohol at boiling point. It required to be dissolved in water, evaporated to dryness, and treated with boiling absolute alcohol *seven times* before all traces of nitrate of calcium—which was obstinately held by the nitrate of strontium—were completely eliminated. Before I tried it I had no idea of the difficulty I should have in getting entirely rid of the calcium. I only considered the calcium was completely eliminated when the residue, after evaporating an aqueous solution of nitrate of strontium *to dryness*, could be completely dissolved in boiling absolute alcohol. I was unable to detect the presence of calcium in this solution. As an experiment, I evaporated to dryness 100 c.c. of the alcoholic solution saturated at boiling-point, and I tested for calcium in the very small residue. For this purpose, I treated it first of all with a mixture of equal volumes of alcohol and anhydrous ether, and, having thus dissolved it, I evaporated the liquid in platinum; then I put the traces left from evaporating the liquid and the dried residue into an oxyhydrogen blowpipe, to examine the spectrum of the flame.

I have no hesitation in saying that the complete separation of the nitrates of calcium and strontium is the most difficult operation I know of. In addition, I tried to check the degree of purity of the nitrate, as I shall describe further on.

The nitrate of strontium, when freed from calcium salts by boiling alcohol, contained a notable amount of sodium, which could only be eliminated by converting the strontium into a carbonate. But nitrate is not suitable for preparing carbonate. When this salt is formed from nitrate it is always more or less granular, as is the case also with sulphate of barium, which retains the nitrate however the washings may be prolonged, and, although in the granular state the carbonate of strontium is easily washed, on the other hand it obstinately retains sodium.

I began therefore by converting the nitrate into carbonate, so that on pouring a dilute solution of this salt into an excess of a solution of sesqui-carbonate of ammonium, and after washing the granular carbonate as completely as possible, I could take it up by dilute hydrochloric acid.

Wishing to ascertain whether this chloride of strontium was quite free from calcium, I evaporated the whole solution to dryness in a platinum retort, and I treated the dehydrated residue, which was a crystalline powder, five times with boiling absolute alcohol, thus adopting M. Bunsen's method of separating calcium. I carefully examined for calcium, on the one hand, the chloride deposited by cooling the decanted boiling alcohol, and, on the other hand, the residue of evaporation of this alcohol after the deposition of the chloride. I was not able to detect, by spectrum analysis of an oxyhydrogen blowpipe flame turned on to these chlorides, any trace of the calcium spectrum, not even of its *green* line, which is never absent when chloride of strontium contains a weighable quantity of calcium.

Having got this negative result, I put all the chloride of strontium into water, and poured the dilute solution into

an excess of a solution of sesqui-carbonate of ammonium. When made in this way, carbonate of strontium is very tenuous; it makes water milky. I had to leave the liquid to settle, sheltered from draughts: this was a very slow process.

I washed the carbonate by decantation; it took about three months to complete the operation on about 200 grms. of carbonate. I only desisted when the decanted water ceased to cloud a dilute solution of nitrate of silver.

In this form carbonate of strontium, when put into a Bunsen flame on a platinum loop, coloured it very deep yellow, and showed the sodium spectrum for a very long time.

I could not use hydrochloric acid for dissolving it, and as for successive precipitations in sesqui-carbonate of ammonium years would not suffice to eliminate all the sodium capable of being thus removed. Besides, by working in this way, one would run the risk of introducing as much sodium from the air as the treatment would be able to eliminate from the carbonate. I therefore applied the method which succeeded so well in removing sodium from the carbonates of lithium and calcium precipitated under identical conditions; that is to say, I treated the carbonate of strontium with water charged with carbonic acid. With this object I put the carbonate into 4 litres of pure water, through which I slowly passed carbonic acid to saturation. After standing for a night, the liquid, though still clouded, was decanted into a platinum vessel and replaced by an equal volume of pure water. I again passed carbonic acid into it for twenty-four hours. I repeated the operation five times; then I put the carbonate into pure water, so long as the liquid, when settled, gave to a flame the slightest sodic characteristic.

The liquids containing carbonate of strontium with carbonic acid were separately boiled in platinum, in order to deposit the carbonate by setting free the acid. After boiling, the water from the first three treatments, after a moderate evaporation, sensibly coloured a flame yellow; the water from the fourth and fifth treatment did not give the sodic character to a flame. The carbonate of strontium deposited by the elimination of the carbonic acid, when put into a flame, gave it the sodium characteristics in every case, but less and less distinctly from the first to the fifth. In the third case the amount of sodium was so far reduced that, when heated in an oxyhydrogen blowpipe, oxide of strontium was formed completely free from sodium; this was not possible in the first two cases.

The bulk of the carbonate of strontium, which had been freed from sodium by means of water charged with carbonic acid, and then by boiling water, when put into a flame on a platinum loop, gave a sodic character temporarily, and not stronger than platinum which has been left for an hour in the air under a bell-jar after having been heated to redness.

After the experiment, the bulk of the carbonate was dried in the platinum vessel, protected from air dust; it was then kept under a bell-jar, in a covered platinum vessel. After being kept for several weeks, the carbonate gave a sodic character to flames, *just as though it had never been purified!*

I converted a small portion of carbonate which had been purified from sodium in an oxyhydrogen blowpipe into solid nitrate, and I mixed part of this salt with two parts of the same carbonate which had been previously freed from all sodic characteristics in an oxyhydrogen blowpipe. This mixture, when put into a conical cup, on a layer of pure oxide of strontium, enabled me to study the luminous spectrum of *coherent* oxide of strontium, much more easily than oxide made from carbonate alone in an oxyhydrogen blowpipe.

I prepared chloride of strontium by means of oxide made from the carbonate and pure chloride of ammonium. For this purpose, after having heated to whiteness a small crucible of pure platinum, I deposited on the bottom of the crucible a layer of pure chloride of ammo-

nium, *made in platinum*, and I poured on it a mixture of oxide of strontium and of the same chloride of ammonium. I covered the crucible and put it into a second platinum crucible, also covered; I then heated it, gently at first, and afterwards sufficiently to drive off all the excess chloride of ammonium, and yet not enough to melt the chloride.

When introduced into a Bunsen flame or an oxyhydrogen blowpipe, when quite fresh, the chloride gave them the sodic characteristics, but very slightly. Nevertheless the sodium line only disappeared completely when the chloride was almost entirely converted into basic oxychloride. Although the sodium spectrum appeared, there was a fundamental difference between the manner in which the very slightly hygroscopic chloride of strontium and the chlorides of lithium and calcium behaved, for the latter, as soon as they were made, gave persistent and strong signs of the presence of sodium.

Having met with great difficulties in preparing compounds of strontium which would not, on spectrum analysis, show any trace of the calcium lines, and especially of the green calcium line, I applied, through a friend, to a firm which prepared metals and salts for spectroscopic use. I must confess that, without exception, all the chloride of strontium thus supplied me contained calcium which I could not separate analytically. I make this statement, not to blame the chemical manufacturers, but to account for the errors into which persons are likely to fall who are obliged to procure commercially those chemicals they cannot prepare themselves, or of which they cannot verify analytically the absolute purity.

(To be continued).

THE COMPOSITION OF WATER. A SHORT BIBLIOGRAPHY.

By T. C. WARRINGTON, B.A.

THE following is a list of papers bearing on the determination of the ratio O : H, arranged in chronological order under the following headings:—

I. Determination of the relative densities of hydrogen and oxygen.

II. Determination of the ratio of the combining volumes of hydrogen and oxygen.

III. Gravimetric methods:—

a. The combination of weighed quantities of hydrogen and oxygen to form water (weighed in some cases).

b. The combination of a weighed quantity of oxygen with hydrogen to form a weighed quantity of water.

c. The combination of a weighed quantity of hydrogen with oxygen to form a weighed quantity of water.

d. Indirectly from the molecular weight of ammonium chloride.

IV. Critical and miscellaneous.

A full bibliography of the earlier papers on the composition of water and of the dispute as to the real discoverer, whether Cavendish, Watt, or Lavoisier, is to be found in the "Critical Account of Water Controversy, with Bibliography," Wilson's "Life of Cavendish," p. 269.

I. Determination of the Relative Densities of Hydrogen and Oxygen.

(1). 1841. DUMAS and BOUSSINGAULT.

"*Récherches sur la véritable Constitution de l'Air Atmosphérique.*"

Ann. Chim. et Phys., (1841), [3], iii., p. 257.

Compt. Rend., (1841), xii., p. 1005 (abs.).

Erdm. J. pr. Chem., (1841), xxiv., p. 64 (translation).

Bibl. Univ., (1841), xxxiii., p. 363.

Liebig Ann., (1841), xl., p. 230.

Pogg. Ann., (1841), liii., p. 391.

During the course of an investigation on air, the density of oxygen relative to dry air is determined to be 1.1057 as the mean of three experiments.

(2). 1845. V. REGNAULT.

"*Sur la Détermination de la Densité des Gaz.*"

Ann. Chim. et Phys., (1845), [3], xiv., p. 211; and xv., p. 512.

Erdm. J. pr. Chem., (1845), xxxv., p. 203.

Compt. Rend., (1845), xx., p. 975.

Pogg. Ann., (1845), lxv., p. 395.

(3). 1879. P. VON JOLLY.

"*Die Veränderlichkeit in der Zusammensetzung der Atmosphärischen Luft.*"

München, Akad. Abhandl., (1880), xiii., (abt. ii.), p. 49.

Wied. Ann., (1879), vi., p. 520.

The densities of oxygen and nitrogen were determined.

(4). 1884. G. AGAMENNONE.

"*Sulla Deformazione Prodotta in Vasi di Vetro da Pressioni interne.*"

Atti (Rend.) della Accad. dei Lincei, (1884-5), [4], i., pp. 665 and 699.

The author calculates the amount and coefficient of deformation of a glass vessel due to internal pressure.

(5). 1888. LORD RAYLEIGH.

"*On the Relative Densities of Hydrogen and Oxygen.*" (Prel. Notice; read Feb., 1888).

Proc. R. S., (1887-8), xliii., p. 356.

Abs. J. C. S., (1888), liv., p. 643.

Chem. News, (1888), lvii., p. 73.

Beibl. Wied. Ann. (1888), xii., p. 411.

Regnault's method is used with additional precautions. Regnault's results are shown to be affected by the shrinkage of the vacuous globe, due to external pressure.

(6). 1888. J. M. CRAFTS.

"*Sur une Correction à apporter aux Déterminations par Regnault du poids d'un Litre des Gaz Élémentaires.*" (Note).

Compt. Rend. (1888), cvi., p. 1662.

Ber., (1888), xxi., Ref. p. 503.

A globe of the same glass as that used by Regnault is employed to find the correction to be applied to Regnault's determination, arising from the shrinkage of vacuous globe. Cf. (5).

(7). 1889. J. P. COOKE.

"*On a New Method of Determining Gas Densities.*"

Amer. Chem. J. (1889), xi., p. 509.

Proc. Amer. Acad. (1889), xxiv., [N.S. xvi.], p. 202.

Abs. J. C. S., (1890), lviii., p. 361.

Beibl. Wied. Ann., (1890), xiv., p. 213.

This method avoids shrinkage of vacuous balloon. The tare of the balloon is found by filling with CO₂, which is displaced by air into an absorption apparatus and weighed.

(8). 1890. J. JOLY.

"*On a Method of Determining the Absolute Density of a Gas.*" (Read June, 1890).

Proc. R. Dublin Soc. (1888-90), vi., [N.S.], p. 534.

Phil. Mag., (1890), [5], xxx., p. 379. (Reprint).

Beibl. Wied. Ann., (1891), xv., p. 153.

The method consists in measuring the gas in one vessel, and compressing into a much smaller stout copper vessel which is used for weighing the gas. A specimen result for dry air is given.

(9). 1890. A. LEDUC.

"*Sur la Densité de l'Azote et de l'Oxygène d'après Regnault, et la Composition de l'Air d'après Dumas et Boussingault.*" (Read Aug., 1890).

Compt. Rend., (1890), cxi., p. 262.
 Jour. de Physique, (1891), [2], x., p. 37.
 Beibl. Wied. Ann., (1891), xv., p. 1.

A comparison between the two sets of observations shows a want of agreement.

(10). 1890. ED. W. MORLEY.

"Ratio of the Densities of Oxygen and Hydrogen."

Proc. Amer. Ass., (1890), xxxix., p. 163.
 Nature, (1890), xlii., p. 530.

The paper is an abstract, giving a sketch of the method, but no results. In the *Nature* report some figures are given.

(11). 1891. A. LEDUC.

"Sur les Densités de l'Oxygène, de l'Hydrogène, et de l'Azote."

Compt. Rend., (1891), cxiii., p. 186.
 Abs. J. C. S., (1891), lx., p. 1416.
 Beibl. Wied. Ann., (1892), xvi., p. 105.

Slight modification of Regnault's method.

(12). 1892. Lord RAYLEIGH.

"On the Relative Densities of Hydrogen and Oxygen,"
 II. (Read Feb., 1892).

Proc. R. S., (1891-2), l., p. 448.
 Chem. News, (1892), lxv., pp. 200 and 206.
 Abs. J. C. S., (1893), lxiv., II., p. 10.
 Beibl. Wied. Ann., (1894), xviii., p. 2.
 Nature, (1892), xlii., p. 101.

Elaborate re determination with results, by a modification of Regnault's method.

(13). 1893. Lord RAYLEIGH.

"On the Densities of the Principal Gases." (Read Mar. 4, 1893).

Proc. R. S., (1893), liii., p. 134.
 Chem. News, (1893), lxvii., pp. 183, 198, 211.
 Amer. Jour. Sci., (1894), [3], xlvii., p. 234. (Abs.).
 Abs. J. C. S., (1893), lxiv., II., p. 514.
 Beibl. Wied. Ann., (1893), xvii., p. 685.

The densities of oxygen and hydrogen are determined and compared with those of other experimenters. Their bearing on the ratio O : H is discussed.

(14). 1893. A. LEDUC.

"Sur les Densités de quelques Gaz et la Composition de l'Eau." (Read May, 1893).

Compt. Rend., (1893) cxvi., p. 1248.
 Beibl. Wied. Ann., (1893), xvii., p. 994.

The author discusses his own results with those of Rayleigh and Morley.

(15). 1893. A. LEDUC.

"Sur le Poids du litre d'Air Normal et la Densité des Gaz." (Read Dec., 1893).

Compt. Rend., (1893), cxvii., p. 1072.
 Beibl. Wied. Ann., (1894), xviii., p. 489.

The accuracy of the method of determining gas-density discussed. Results given for air and nitrogen.

(To be continued.)

Properties of Metals extracted from their Amalgams.—M. Guntz.—Melted metals, as we know them, probably consist of very condensed molecules formed, with a liberation of heat, from their atomic state. This causes the properties of such metals not to agree with their thermic constants. Thus manganese, the oxidation heat of which (98.6 cal.) is close to that of the alkaline metals, is but little affected by the air when melted. These considerations explain the chemical activity of metals extracted from their amalgams at low temperatures.—*Comptes Rendus*, cxxii., No. 8.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 5th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. Alexander Simpson, Joseph John Bowley, Walter A. Voss, and William A. Bone were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Percival Jenkins, 30, St. John's Road, Clifton, Bristol; Tom Mitchell, Cemetery House, Shaw, near Oldham; Raymond St. George Ross, 30, Britannia Square, Worcester.

Of the following papers those marked * were read:—

*29. "*The Explosion of Cyanogen.*" By H. B. DIXON M.A., F.R.S., E. H. STRANGE, B.Sc., and E. GRAHAM B.Sc.

Since it has been shown by previous investigators that cyanogen probably burns first to carbonic oxide, and secondly to carbon dioxide, both in ordinary flames and in the explosion wave, and since the burning of carbonic oxide to carbon dioxide appears to be generally conditioned by the presence of water vapour, it seemed of interest to investigate the course of the chemical changes occurring in the complete combustion of cyanogen.

The authors first measured the rate of explosion of cyanogen with an excess of oxygen. The conclusion drawn is that when cyanogen is exploded with its own volume of oxygen it burns directly to carbonic oxide; on adding a second volume of oxygen to the mixture, carbonic oxide is formed in the wave front, and the heated carbonic oxide and oxygen combine behind the wave-front; on adding more oxygen the formation of carbon dioxide is sufficiently rapid to affect the velocity of the wave itself. When one volume of cyanogen is exploded with four volumes of oxygen, the rate is 5 per cent faster than the rate calculated on the supposition that the cyanogen is only burning to carbonic oxide in the wave-front. The formation of carbon dioxide, although without influence on the velocity of the wave in the faster explosions, is found to exert an influence in the slower explosions.

In order to study the intensity and duration of the flame following the explosion wave, photographs were taken of the jets of flame projected from the ends of long tubes filled with the explosive mixtures of cyanogen and oxygen. Since the wave travels faster than sound in the unburnt gas the wave-front must reach the end of the tube before any other disturbance can be propagated through the gas; the jet of flame which is driven from the tube must accordingly be part of the column of burning gases following in the wake of the wave. When cyanogen is burnt with its own volume of oxygen to carbonic oxide, the intensity of the explosion is very great, but only a very slight jet of flame is projected from the tube. The length of column of highly heated gases must be short. But when cyanogen is burnt with twice its volume of oxygen to carbon dioxide the explosion is less intense, but the jet of flame projected from the tube is long and of considerable brightness. The column of highly heated gases must therefore be long. If the extra oxygen is inert in the wave-front it accounts for the superior brilliancy of the unimpeded reaction $C_2N_2 + O_2 = 2CO + N_2$ over the impeded reaction $C_2N_2 + 2O_2 = 2CO + O_2 + N_2$, and if the formation of carbon dioxide mainly occurs behind the wave, it accounts for the brightness of the jet of still burning gases thrown from the tube in the second case.

To obtain a direct record of the intensity and length of flame in the two cases, the explosion wave was photographed on a very rapidly moving film as it passed a short window in a long tube. The sensitive film was fixed round a light iron drum driven by a high speed electric

motor. Two tubes, each provided with a window, were fixed side by side, one being filled with one mixture, the second with the other. The gases being fired simultaneously, the two flames were photographed on the same film. On developing the film in a long trough each image received precisely the same treatment, and one could be compared with the other.

The front of the flame in all cases was sharply defined, but the rear of the flame dies away in a tail which gradually thins out. When cyanogen is exploded with its own volume of oxygen, an intense image of the window is produced, only slightly drawn out by the revolution of the drum, followed by a faint and short tail. When, however, cyanogen is exploded with twice its volume of oxygen, the image is not so bright and there is no abrupt fall in intensity; the tail is much brighter and longer. These photographs accord with the view that cyanogen burns first to carbonic oxide, and that the formation of carbon dioxide is a secondary action.

Photographs were then taken with the same apparatus of the flames produced by mixtures of cyanogen with two vols. of oxygen (1) well dried, and (2) moist. No difference could be detected in the images of the flames. Water-vapour, therefore, does not seem to affect the reaction between oxygen and the just-formed carbonic oxide. Similar photographs of the flames produced in mixtures of carbonic oxide and oxygen in the dry and moist state showed a marked difference; in the presence of steam the flame is intenser and shorter.

*30. "On the Mode of Formation of Carbon Dioxide in the Burning of Carbon Compounds." By H. B. DIXON, M.A., F.R.S.

Assuming that in the combustion of carbon compounds the carbon burns first to carbonic oxide, the author discusses the views that have been advanced concerning the function of steam in promoting the union of carbonic oxide and oxygen.

Professor Armstrong considers that the moisture acts as an electrolyte, and that chemical change only takes place when carbonic oxide, steam, and oxygen are in contact. The chief difficulty in this theory is to account for the great velocity with which the explosion wave is propagated through a damp mixture of carbonic oxide and oxygen. In gaseous mixtures the rate of explosion approximates to the rate of the forward movement of the reacting molecules, *i.e.*, the wave is transmitted like sound from molecule to molecule. According to the electrolytic theory, the chemical change could only occur on the simultaneous collision of at least three molecules; yet the explosion wave is propagated in carbonic oxide, steam, and oxygen at a rate of 1738 metres per second. In the explosion of cyanogen, carbon dioxide is formed without the intervention of steam. This theory, which has the advantage of including a number of cognate phenomena, seems better suited to explain reactions at ordinary temperatures than those occurring in the explosion wave.

A similar difficulty occurs in Professor J. J. Thomson's theory, according to which the steam, by forming liquid particles, produces dissociation of the oxygen molecules, and thus facilitates the oxidation of the carbonic oxide. It is hard to understand how steam, which is far below the saturation point at ordinary temperatures, can be condensed in the explosion wave.

Mendeleeff considers that carbonic oxide cannot combine directly with oxygen because all combination between gases takes place according to the law of equal volumes. Carbonic oxide and steam react in equal volumes, and therefore the change begins by the carbonic oxide taking the oxygen from the steam. The liberated hydrogen unites with its own volume of oxygen to form hydrogen peroxide, and this in turn reacts with its own volume of carbonic oxide to form carbon dioxide and water. The spark will not, however, kindle a mixture of dried carbonic oxide and nitrous oxide (mixed in equal volumes), but the addition of a trace of steam renders the mixture explosive.

Lothar Meyer and Beketoff attribute the influence of the steam to the fact that the direct action of carbonic oxide on oxygen requires a very high temperature, whereas carbonic oxide decomposes steam much more readily. But although it may be true that steam facilitates the oxidation of carbonic oxide on account of the low temperature of the reaction, this does not account for the non-union of carbonic oxide and oxygen at the intensely high temperature produced in the wave-front in the explosion of cyanogen.

The author shows that a dried mixture of carbonic oxide and ozonised oxygen is not inflamed by the spark; here the resistance cannot be attributed to the stability of oxygen.

The author has repeated Beketoff's experiment of exploding together a mixture of cyanogen, carbonic oxide, and oxygen in the dry state. With quantities of cyanogen below 12 per cent the flame causes an *incomplete* combustion of the carbonic oxide. The same results were obtained when carbon bisulphide was substituted for cyanogen. The more intense the exciting flame, the larger was the amount of carbonic oxide burnt.

The dissociation of carbon dioxide, held by Bunsen and by Deville to limit the combustion of carbonic oxide and oxygen, may be the reason why carbonic oxide and oxygen do not unite in the wave-front, but can combine as the gases cool down behind the wave. The reaction between steam and carbonic oxide gives out little heat, so carbonic acid might be formed indirectly, and the liberated hydrogen might re-form steam, which could exist at a temperature at which carbonic acid would be broken up. The union of dry carbonic oxide and oxygen, without flame, on the surface of platinum, may be due partly to the power of the metal to conduct away heat.

The dissociation theory explains some of the facts observed concerning the combustion of carbonic oxide, but probably some other cause exists which limits the union of carbonic oxide and oxygen at lower temperatures.

The Röntgen rays do not appear to make a dried mixture of carbonic oxide and oxygen inflammable.

*31. "On the Explosion of Chlorine Peroxide." By H. B. DIXON, M.A., F.R.S., and J. A. HARKER, D.Sc.

The decomposition by shock of endothermic compounds, discovered by M. Berthelot, and the explosion of carbon bisulphide vapour described by Dr. Thorpe, led the authors to determine whether a true explosion-wave was transmitted through these compounds. It was found, however, that when a charge of fulminate was fired in a steel bomb attached to a long tube filled with cyanogen or acetylene, the detonation was not transmitted through the gas in the tube except for a short distance. With carbon bisulphide the flame extended for some distance, but gradually died out. M. Maquenne has recently obtained similar results.

A mixture of chlorine peroxide and oxygen (with a trace of chlorine) was prepared by warming potassium chlorate with sulphuric acid. The gases were passed up through a long glass tube, 33 ft. long, inclined at an angle of 30°. When the tube was full, "bridge-pieces" were clamped on at each end. The explosion was started by igniting a mixture of hydrogen and oxygen in one bridge-piece. The explosion-wave set up in this was communicated to the chlorine peroxide. By making the explosion break a silver bridge (coated with paraffin) at each end of the tube, the rate of the explosion was determined on the electric chronograph. A sample of the gas for analysis was collected at the end of the tube.

In two experiments the following results were obtained:—

	Composition of mixture.	Rate of explosion in metres per second.
1.	$\left\{ \begin{array}{l} \text{ClO}_2 \dots \dots 53.5 \\ \text{O}_2 \dots \dots 46.5 \end{array} \right\} \dots \dots$	1065
2.	$\left\{ \begin{array}{l} \text{ClO}_2 \dots \dots 64.0 \\ \text{O}_2 \dots \dots 36.0 \end{array} \right\} \dots \dots$	1126

It would appear, therefore, that a true explosion-wave is propagated through chlorine peroxide.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, March 13th, 1896.

Prof. CAREY FOSTER, Vice-President, in the Chair.

Mr. J. H. REEVES read a paper on "*An Addition to the Wheatstone's Bridge for the Determination of Low Resistances.*"

The piece of apparatus described can be used for measuring the resistance of metre lengths of wires of low resistance, the only additional apparatus required being a sensitive galvanometer, a Post-Office form of resistance-box, and a metre bridge. It differs from the ordinary Kelvin bridge in that, instead of balancing by varying the length of the standard wire between the two contacts, the distance between these contacts is maintained constant, as is also the length of the wire which is being measured, and balance is obtained by altering other resistances in the network. The author has made a number of tests which show that by his arrangement the resistance of metre lengths of copper wires between the limits of No. 22 S.W.G. and a standard cable of 7 No. 16's can be determined with an accuracy of 0.1 per cent.

Mr. REEVES also read a "*Note on the Exact Value of Matthiessen's Standard.*"

Prof. A. GRAY (communicated) said that the author had in his arrangement combined the fixed standard employed in Matthiessen and Hocking's modification of the ordinary bridge with the greater celerity of working arising from the smaller number of operations to be performed when the Kelvin bridge is used. Prof. Gray thinks that he, and probably others, have used a method similar to that of Mr. Reeves, but that the paper is of great utility since it shows how time may be saved and existing apparatus utilised.

Prof. AYRTON said that the advantage of the method described lay in the fact that it was independent of the resistances at the contacts. In Carey Foster's method, however, the coils had to be interchanged, and inaccuracy might be introduced owing to the varying resistance of the mercury contacts. Unless the mercury cups and the copper plates at the bottom were cleaned every day, and the contacts re-amalgamated, the resistance of the mercury cups was very variable. With regard to the question of Matthiessen's standard, it is to be remembered that the specific conductivity of copper has been steadily increasing. This increase was particularly noticeable in the copper prepared by the Elmore process, where, during the deposition of the metal, an agate burnisher is kept continually passing over the surface. Fitzpatrick had explained the rise in conductivity of copper by supposing that the density of the copper now supplied was greater than that of the copper used by Matthiessen, and this explanation seemed quite satisfactory. Mr. Reeves' experiments, however, have conclusively shown that this is not the true explanation; it was now possible to obtain copper in large quantity having a conductivity of 103 on Matthiessen's scale.

The Chairman (Prof. CAREY FOSTER) explained how, when using his method, the accuracy of the result depends not on the elimination of the small resistances at the mercury cups, but on the constancy of these resistances. Matthiessen and Dr. Russell found that the specific gravity of copper was apt to be low, on account of the presence of dissolved oxide, and they were the first to pass hydrogen gas through the molten metal to remove this oxide.

Mr. APPLEYARD gave a simple diagrammatic sketch of the author's arrangement, and also pointed out that

better results would probably be obtained with a galvanometer of 1 or 2 ohms resistance.

Mr. CAMPBELL said that it ought to be definitely settled whether Matthiessen's standard was the conductivity per unit volume or per unit mass. Since copper was always bought by weight, he, as a practical man, strongly advocated the adoption of the mass conductivity; further, in this case the measurement of the specific gravity would be avoided.

Mr. Reeves replied.

A communication, by Herr PULUJ, "*On Kathode Rays*" was read by the Secretary.

Herr Puluj exhibited some Röntgen photographs taken by means of a form of Crookes tube which he had described in a memoir published in 1889. With this tube he has succeeded in obtaining impressions with exposures of only two seconds.

Herr Puluj considers that the particles of matter torn from the kathode, which convey negative electrostatic charges, by impact on the glass walls or on screens, equalise their electric charges, and in this process call forth not merely a disturbance of the material molecules, but also of their ether envelopes. Each portion of the glass or screen bombarded by the kathode stream becomes the starting-point of ether waves, which, according to their oscillation period and oscillation character, are either visible rays (phosphorescence) or invisible Röntgen rays. The oscillations of the invisible rays may take place in the longitudinal direction, but no convincing argument has up to now been brought forward to support this view.

The Secretary also read a "*Note on Permeability to Röntgen Rays,*" by Messrs. ACKROYD and KNOWLES.

The authors have exposed a plate on which a number of pieces of metal, oxides, and sulphates were placed to the Röntgen rays in order to see whether the permeability of bodies to these rays depends on the atomic or molecular weight of the body. In each case it was found that the opacity increased with the molecular weight.

Mr. BLAKESLEY said that he considered the Röntgen rays to be the propagation of electrostatic strain through space. With reference to the non-refrangibility of these rays, he had observed in one of the photographs exhibited by Mr. Swinton a dark line at the edge of the shadow of a wooden pencil, which might have been due to the refraction of the rays by the wood. Mr. Blakesley has, however, found that this line is due to the varnish on the pencil. Some Röntgen photographs of quartz and ebonite rods not only did not exhibit these dark lines, but there was a very slight indication of a bright line just on the edge of the shadow, which would indicate that the refraction of these rays was less in the rods than in the surrounding medium.

Mr. EDSER exhibited some photographs taken with Mr. Jackson's form of tube, in which a concave kathode is employed. Mr. Edser said that the whole of the tube on the kathode side of the anode plate phosphoresced, so that the Röntgen rays seem to partake of the character of diffused light.

Prof. AYRTON said Mr. Jackson had found that the kathode rays form a parallel beam, and do not first come to a focus and then again spread out.

The CHAIRMAN said some observations made by Mr. Porter agreed with those of Mr. Edser.

Mr. BLAKESLEY described the tube used by Puluj, in which a mica screen coated with green calcium sulphide is placed between the kathode and the anode.

Mr. GARDNER said that there seemed to be some confusion, for when a concave kathode is employed, the kathode rays are brought to a focus and then again diverge. The phosphorescence on the inside of the glass had been shown by Lenard to be due to electricity travelling round the inside surface of the glass.

Mr. PIDGEON asked if any one had tried the effect of mounting the photographic film on a metal plate.

The CHAIRMAN said that Captain Abney had found that if the film was mounted on a ferrotype plate no action took place.

Prof. PERRY said he, for one, was of opinion that the Röntgen rays were undulatory. Prof. Larmor had given an explanation which seems to agree with the observed facts. This explanation supposes that the intermolecular spaces respond to vibrations of a certain frequency. The reason no refraction or diffraction effects had been observed was probably because of the extreme smallness of the wave-length of the undulation.

After some further remarks by some of the members the Society adjourned till March 27th.

NOTICES OF BOOKS.

Food and Sanitation. Vol. VII., No. 180, February 29, 1896.

THE foreign relations of *Food and Sanitation* appear to be in a state of tension. It has a *casus belli* against the *Lancet*, dating as far back as 1893, relating to Valentine's "meat juice," and another concerning the *Lancet's* commission on lamps and mineral oils. There is also a delicate innuendo on "blackmail and its results." With these disputes we have certainly no call to interfere.

We must, however, agree with *Food and Sanitation* in pronouncing 73° F. not a safe flashing-point for mineral oils, especially in view of the late serious accidents.

In the leader entitled "The *Lancet* on its Defence" we notice passing commendation of a certain "Sewage Purification Company." Now we can understand international copyright, international patent-right, or even international arbitration; but by what logical *tour de force* a process for sewage treatment can be called "international" is inconceivable.

But *Food and Sanitation* is at war also with the *Daily Chronicle*, with the National Health Society, and Mr. Ernest Hart. Who is wrong and who is right in these differences of opinion we cannot examine. Our contemporary deserves, however, the support of the public for its outspoken position as regards the adulteration of food, a subject on which British law is lamentably weak.

Aluminium. Manchester: The Aluminium Supply Company, 38, Victoria Buildings.

WE have here a small book setting forth the properties and applications of a metal which is deservedly claiming an increased share of attention. The metal aluminium is here called sometimes *aluminum* and sometimes *alium*, an unpleasant *alias* which is here considered necessary in these days of hurry and scurry. Because the electric power utilised in the production of aluminium by means of energy derived from the Niagara Falls, the author thinks he may be pardoned for introducing into a mechanical work a few views of the Falls—a somewhat threadbare addition.

We find here an account of the composition and forms of the "alium" supplied by the Pittsburgh Reduction Company under the patents of Charles M. Hall. The percentage of actual aluminium in the alium is stated as 99.75 to 99.25 per cent, though they have in stock metal at 99.90 per cent. The author speaks of the resistance of the metal to oxidation and corrosion. Its usual impurities are said to be silicon and iron. Of sodium, which has of late been detected in samples of aluminium prepared electrolytically, and which seriously interferes with the useful properties of the metal, nothing is said. The author speaks of the strength of the metal, its solubility, its galvanic action, and place in the electro-chemical series. Here we find the very necessary caution that "alium" exposed to liquids should not come in contact with any other metal, as the metal is then liable to be

impaired by electric action. A similar caution must apply to alloys and to impurities of the metal. The applications of "alium," actual and prospective, are described without any exaggeration.

The difficulty of soldering aluminium has not been overlooked, but it is stated that the Pittsburgh Company supply a special solder and flux which greatly overcome the difficulties.

We regret to note that no instructions are given for the analysis of commercial samples of aluminium. Information of such a kind would have been much more to the purpose than tables of the areas and circumferences of circles which have no special reference to aluminium, and which, as they fill up quite one-tenth of the book, can scarcely be regarded as other than "padding."

Intensity Coils, how Made and how Used: also Electric Light, Telephone, Phonograph, &c. By "DYER." Seventeenth Edition. London: Perkin, Son, and Rayment, 99, Hatton Garden. Pp. 138.

THIS is a clearly written and abundantly illustrated little volume. From the mere fact that it has gone through seventeen editions we may infer how widely it has been appreciated.

To the amateur, and to the incipient electrician who aims at learning by experiment, we know of no book which we could recommend in preference.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 8, February 24, 1896.

Radiations emitted by Phosphorescence.—Henri Becquerel.—In a former Session, Ch. Henry announced that phosphorescent zinc sulphide interposed in the track of rays emanating from a Crookes tube augments the intensity of the radiations traversing aluminium. On the other hand, M. Nievenglowski has observed that commercial phosphorescent calcium sulphide emits radiations which traverse opaque bodies. This fact extends to various phosphorescent substances, and especially to uranium salts, the phosphorescence of which has a very brief duration. I have been able to perform the following experiment with double uranium and potassium phosphate:—We enclose a Lumière photographic plate (gelatino-bromide) in two folds of very thick paper, so that the plate does not become shaded on exposure to the sun for a day. We place on the outside of the sheet of paper a plate of the phosphorescent substance, and expose the whole to the sun for several hours. When we then develop the photographic plate, we find that the silhouette of the phosphorescent substance appears in black on the proof. If we interpose a coin between the phosphorescent substance and the paper we see its image appear on the proof. We may repeat the same experiment by interposing a thin plate of glass between the phosphorescent substance and the paper, which excludes the possibility of a chemical action due to vapours which might emanate from the substance heated by the rays of the sun.

Manganese Carbide.—Henri Moissan.—The carbide, CMn_3 , discovered by Troost and Hautefeuille may be produced at temperatures between 1500° and 3000°. When pure, it decomposes water at ordinary temperatures, giving a mixture of methane and hydrogen in equal parts.

Nickel and Cobalt Boride.—Henri Moissan.—The nickel and cobalt borides, BoNi and BoCo , are easily ob-

tained in a crystalline state at 1200°. These novel compounds have properties analogous to those of iron boride, previously described. They enable us to introduce boron into such metals as iron, since at a high temperature boron and silicon expel carbon from melted cast iron.

Determination of Arsenic.—Armand Gautier.—(See p. 134).

Process used to Confer Immunity against the Bites of Serpents.—D'Abbadie (from documents furnished by Sr. de Serpa Pinto).—The patient is inoculated with the venom of the Alcatifa, a venomous serpent of East Africa. After the operation the person takes an oath never to kill a venomous serpent.

Transformation of Dextro-camphoric Acid into Dextro-camphor. Partial Synthesis of Camphor.—A. Haller.—The author has no doubt of the identity of the camphor derived from camphoric acid with ordinary camphor.

Volumetric Analysis of a Mixture of Chlorides, Hypochlorides, and Chlorates.—Ad. Carnot.

Analysis of a Mixture of Chlorides, Chlorates, and Perchlorates.—Ad. Carnot.—These two papers will be inserted as soon as practicable.

Production of Röntgen's Silhouettes.—Ch. V. Zenger.—In the abstract of my paper inserted in the *Comptes Rendus* it was not mentioned that the successful proofs sent by me had been obtained in the laboratory of the Slavic Polytechnicum, of Prague, between the 11th and the 22nd of January. They were taken by Domalip, professor of electrotechnics at this school, in concert with Brozet, demonstrator of physics. The interesting point is that Domalip has obtained electric images on the plate by means of plates of copper, brass, zinc, lead, and steel. This is, in my opinion, the proof that there is here merely a phenomenon of electric induction producing phosphorescence of the gelatin, and at the same time an electric discharge in the gelatin; and, lastly, the fluorescence of the ambient air, and, as in case of the dark discharge, of the electricity. In my opinion, these are the three agents which determine the decomposition of the silver salts in the sensitive layer. There are no special radiations, no X rays, and no dark light.

Action of the X Rays upon the Diamond.—Abel Buguet and Albert Gascard.—Already inserted.

Cause of the Invisibility of Röntgen's Rays.—MM. Darieux and De Rochas.—This and the five following papers will be inserted in full.

Röntgen's Rays.—Georges Meslin.

Some Properties of Röntgen's X Rays.—H. Dufour.

Emission of Röntgen's Rays by Tubes containing a Fluorescent Substance.—M. Piltchikoff.

Certain Properties of the Dark Light.—Gustave le Bon.—(See p. 121).

Photography through Opaque Bodies.—A. and L. Lumière.

Action of some Hydrogen Compounds upon Sulphuryl Chloride.—A. Besson.—Not suitable for abridgment.

Yield of various Volatile Wood Oils in Charcoal: Methylic Alcohol and Acetic Acid.—Ernest Barillot.—This memoir requires the accompanying figure.

Temperature of the Sparks produced by Uranium.—M. Chesneau.—These sparks ignite, not merely coal-gas (much more easily than sparks of iron), but also wicks of cotton saturated with ethylic alcohol at 90 per cent, benzene, and petroleum essence. The author proposes to utilise this property for lighting lamps.

New Method of Forming Nitro-prussides.—C. Marie and R. Marquis.—The authors' experiments show that we may pass from hydroferrocyanic acid to nitro-prussic acid by the elimination of a mol. of hydrocyanic

acid and substituting a NO group and an atom of hydrogen.

Crystalline Ammoniacal Chromous Carbonate.—Georges Baugé.—The author has obtained, by general methods, a new compound, $\text{CO}_3\text{Cr}, \text{CO}_3(\text{NH}_4)_2\text{H}_2\text{O}$. This is the first double ammoniacal salt of chromous oxide.

Veratrylamine.—Ch. Moureu.—This compound is easily obtained by acting upon veratrol with ordinary nitric acid.

Thermochemical Study of Orthochlorobenzoic Acid and some of its Derivatives.—Paul Rivals.—Not suitable for abstraction.

Conversion of the Solution of Liquid Formaldehyd into Vapours for Disinfection.—A. Trillat.—The volatilisation of liquid formaldehyd can be effected without the introduction of deleterious gases, such as carbon monoxide, effecting the destruction of the most various pathogenic microbia.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements after Easter:—Professor James Sully, of University College, London, three lectures on "Child-Study and Education"; Mr. C. Vernon Boys, three lectures on "Ripples in Air and on Water"; Professor T. G. Bonney, two lectures on the "Building and Sculpture of Western Europe" (the Tyndall Lectures); Professor Dewar, three lectures on "Recent Chemical Progress"; Mr. W. Gowland, three lectures on the "Art of Working Metals in Japan"; Dr. Robert Munro, two lectures on "Lake Dwellings"; Professor W. B. Richmond, R.A., three lectures on the "Vault of the Sixtine Chapel"; Mr. F. Corder, Curator of the Royal Academy of Music, three lectures on "Three Emotional Composers"—Berlioz, Wagner, Liszt (with musical illustrations); Mr. E. A. Wallis Budge, of the British Museum, two lectures on "The Moral and Religious Literature of Ancient Egypt." The Friday evening meetings will be resumed on April 17th, when a discourse will be given by M. G. Lippmann, on "Colour Photography"; succeeding discourses will probably be given by Professor G. V. Poore, Colonel H. Watkin, C.B., Professor Silvanus P. Thompson, Professor J. A. Ewing, Professor J. A. Fleming, and other gentlemen.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Medical, 8.30.

TUESDAY, 24th.—Royal Institution, 3. "The External Covering of Plants and Animals—Its Structure and Functions," by Prof. Charles Stewart, M.R.C.S.

— Medical and Chirurgical, 8.30.

— Institute of Civil Engineers, 8.

— Photographic, 8.

— Society of Arts, 8. "The Colonies and the Supply of Dairy Produce and Products of Petite Culture," by Charles R. Valentine.

WEDNESDAY, 25th.—Society of Arts, 8. "Our Food Supply, as affected by the Farming of the Future," by Prof. James Long.

— British Astronomical, 5.

— Geological, 8.

THURSDAY, 26th.—Royal Institution, 3. "Masters of Modern Thought—IV. Spinoza," by The Rev. W. Barry, D.D.

— Institute of Electrical Engineers, 8.

— Society of Arts, 8. "Kashmir—its People and its Products," by Walter R. Lawrence, C.I.E.

— Chemical, 8. (Anniversary Meeting). President's Address, Election of Officers and Council.

FRIDAY, 27th.—Royal Institution, 9. "New Researches on Liquid Air," by Prof. Dewar, F.R.S.

— Physical, 5.

SATURDAY, 28th.—Royal Institution, 3. "Light," by Lord Rayleigh, F.R.S., &c.

THE CHEMICAL NEWS.

VOL. LXXIII., No. 1896.

ON SOME SPECIMENS OF GLASS EXPOSED TO THE ACTION OF THE X RAYS.

By V. CHABAUD.

Six specimens of glass of different compositions were cut to the thickness of $\frac{1}{100}$ m.m. Of each specimen I made three rectangular plates. Upon a card of the dimension $\frac{1}{2}$ m.m. I cemented six small plates of platinum of $\frac{1}{20}$ m.m. in thickness and 2 m.m. in width.

Upon each platinum plate I arranged two plates of the same specimen, so as to have at the middle two thicknesses. Transversely in the midst, and perpendicular to the two former, I placed the third plate. This arrangement enabled me to have at the centre three thicknesses, i.e., 1.35 m.m., at each side of the centre two thicknesses—that is, $\frac{1}{10}$ of a m.m.—and at the four extremities a single thickness, or $\frac{1}{100}$.

This arrangement was placed on a case of wood containing the photographic plate. The whole covered with a black paper to prevent the direct action of the light emitted by the Crookes tube and of the diffused light of the piece upon the glasses submitted to experiment. The samples of glass themselves had been kept in darkness for two days.

The Crookes tube was placed with its side at 20 c.m. from the surface of the case. The current which passed into the induction coil was furnished by three accumulators; one ammeter placed in the circuit indicated 5 ampères.

The duration of the experiment was sixty minutes.

The Crookes tube was covered outwardly up to the level of the plane passing by the surface of the kathode with a tin paper—the arrangement of Hurmuzescu, in order to augment the yield of the tube.

The six specimens submitted to experiment were the following:—

- | | | |
|----------------------------|----|---|
| Fluorescence (water-green) | A. | Glass with a base of soda, potash, and lime. |
| " (blue) .. | B. | Crystal. |
| " (pale water-green) .. | C. | Ternary glass, with a base of soda, potash, and lime. |
| " (yellowish green) .. | D. | German glass. |
| | E. | Light uranium glass. |
| | F. | Dark uranium glass. |

The proof, when developed, enabled us to see that:—

1. The three glasses A, C, D are the most permeable to the Röntgen rays, and this permeability is very great.
2. Crystal is refractory.
3. The two specimens of uranium glass are traversed with more difficulty than the three glasses A, B, and D.
4. The dark uranium glass was more refractory than the pale uranium glass.

The opacity of crystal glass is easily explained by the presence of lead. The slight transparence of uranium glass can be explained only by admitting the presence of foreign substances, possibly arsenic.

We may also find in these results an explanation of the fact already noticed, that glasses with a blue fluorescence do not give the Röntgen rays, or only to a slight extent.

This may be because the wall of the tube opposes the passage of these rays. The seat of the emission of the Röntgen rays would therefore be in the interior of the tube.—*Comptes Rendus*, cxxii., p. 603.

ON THE USE OF ARTIFICIAL HEXAGONAL BLENDE AS A SUBSTITUTE FOR THE CROOKES PHIALS.

By M. TROOST.

ARTIFICIAL blende, which we obtained in concert with Henri Sainte-Claire Deville, in 1861, in the form of hexagonal prisms, transparent, colourless, or slightly yellowish, is capable, as it is known, of acquiring a very fine fluorescence under the influence of the solar light, or of the magnesium flame.

I thought that specimens of these crystals permanent in air and light, and easy to prepare by the procedures which we have laid down (*Comptes Rendus*, lii., p. 983; and *Annales de Chimie et de Physique*, Series 4, vol. v., p. 120), might serve as substitutes for Crookes phials in a great number of experiments which are being made at present on the X rays.

To satisfy myself, I placed a silver gelatino-bromide plate in one of the opaque cardboard boxes which MM. Lumière use for preserving their sensitised plates. I then placed upon this plate, covered with paper, certain perforated metallic objects, a watch-chain, &c., and the box was closed with its opaque cover.

Under these conditions the photographic plate was secure from the action of ordinary light. The specimen of crystals (hexagonal) of blende was fixed by means of plugs of wadding in a metal box closed with a plate of glass applied on the cardboard box containing the photographic plate and the metallic objects.

As the sun did not shine during the experiments, the hexagonal blende was rendered phosphorescent by the combustion of a slip of magnesium, and the whole was kept in darkness. The plate, when developed afterwards by the ordinary procedures, gave a very fine negative, with which I afterwards obtained the very strong negative which I submit to the view of the Academy.

These results, which confirm the hypothesis of our colleague, H. Poincaré, and the experiments recently made by various *savants*, and especially by our colleague H. Becquerel, by Nievenglowski, and Charles Henry, enable us to substitute, if needful, by a simple apparatus, easy to manage, and of an unlimited permanence, the phials of Crookes which require the use of electric currents and a Ruhmkorff coil. These phials are also readily frangible, and are rendered useless by a current too prolonged or slightly too intense.

They require, further, the absolute immobility of the electric apparatus and of the object to be photographed during the whole time of exposure, which limits its applications, especially for surgical diagnosis in living beings.

The metal box containing the artificial hexagonal blende, on the contrary, may be fixed, as also the silver gelatino-bromide plate, by a suitable bandage to the hand, e.g., to be photographed without interfering with the displacement of the rest of the body.—*Comptes Rendus*, cxxii., p. 564.

"Argon and Newton—a Realisation" is the title of a new volume from the pen of Lieut.-Colonel W. Sedgwick, of the Royal Engineers. It is published by W. B. Whittingham and Co. (Ltd.), of "The Charterhouse Press." It is a book for Students of Chemistry Problems, (286 pages, price 7s. 6d.)

THE RÔLE OF THE VARIOUS FORMS OF ENERGY IN PHOTOGRAPHY THROUGH OPAQUE BODIES.

By R. COLSON.

SINCE the discovery of the X rays very numerous experiments have been performed in the search for new means of acting on photographic plates through opaque bodies. Hence there results at present a certain confusion which we can remedy only by a very definite classification of the various effects produced on the sensitive surface of the different forms of energy. In the present paper I purpose summarising the rules to be formulated according to known results, and according to my own observations.

These forms of energy may be classified as:—Mechanical, chemical, thermic, and luminous; there is perhaps room to add the electric form when we have determined its direct influence without the transformations which carry back its effects to one of the foregoing. We must further classify separately the X rays until we have decided upon their real nature.

1. The mechanical action consists in pressure or friction exerted by hard substances in contact with the plate, and shown, on development, by black marks.

2. It is easy to distinguish a chemical action; in every case we may foresee the result according to the nature of the substances present. The contact of a substance capable of producing blackness by the reduction or transformation of a compound of silver acts especially if moisture intervenes. For instance, the humidity which arises from heating a proof in contact with the plate may contain variable proportions of the developer or of hyposulphite. But a chemical influence may also be produced in dryness. I will mention, as an instance, the contact of dry insect, which, as I have found, de-sensitises the stratum by the oxidation of the organic matter, and economises the light on development. It is the same whenever this substance is oxidised.

3. Dry heat is capable of determining the preliminary work which the revealer completes by blackening the proof.

If the plate is wrapped in several thicknesses of black paper, or placed near a source of heat (*e.g.*, an arc lamp), we find that certain parts of the surface are covered and remain light in a revealer which veils the other parts.

I apply on a plate in a camera obscura a card in which I have cut out letters, and expose it for five minutes to watery vapour at about 35°; the gelatin shows the letters in relief in the places which have least undergone the influence of the steam, and in hollows in those which had been most exposed to steam and to heat. The veil of development leaves the letters clear, those especially which were hollow.

A plate is first treated with steam, as in the foregoing experiment, and then heated to 40° for a minute. The letters of moist gelatin undergo incipient fusion, form a decided hollow on drying, and still remain lighter in the revealer.

I lay on a plate three pieces of silver of 2 fcs., carefully cleansed to prevent any chemical action; the whole is wrapped in black paper and kept for two hours on the marble of a "calorifère" at about 40°, with a weight of 1 kilo. upon one of the pieces. On developing, this piece comes out light with a black margin caused by the pressure. The other pieces give nothing.

Thus, in fine, on those parts of the plates rendered moist by the steam given off by the wrapping, or by the vapour escaping from the gelatin, and which is imprisoned on its surface by a body in contact, the heat produces a modification which leaves these parts clear in the revealer; the effect is heightened by the rise of temperature.

This influence is important, for it tends to manifest itself when we employ the direct rays of the sun or the

light of burning substances; that is, in a great number of cases.

4. The ultra-red radiations, if sufficiently intense, act upon the plate like the visible radiations.

For the visible radiations we must take account of the property which the plate possesses to accumulate successive effects, whilst the eye is saturated in the fraction of a second. Behind a board of pine-wood, of 5 m.m. in thickness, I applied a Lumière plate (blue), protected and maintained by four sheets of black paper glued to the wood. After an exposure of eight hours to diffused daylight, I obtained a good proof, showing the structure of the wood and giving a negative of a proof on paper interposed between the plate and the board; tin paper was slightly permeated, and black paper not at all. I satisfied myself that under these conditions of lighting it would be necessary to reduce the thickness to less than 3 m.m. for the eye accustomed to darkness to perceive the light through. The luminous rays may, therefore, in time act upon the plate in a manner appreciable through bodies which we call opaque.

Cornu has shown, in 1880, when studying the reflective power of various metals, that it is possible to observe by fluorescence the very refrangible ultra-violet radiations through a plate of silver deposited chemically and sufficiently thick to arrest the rays of the sun; the transparency is especially observable near the ray R. M. de Chardonnet has utilised this property of silver for photographing objects apparently invisible, and has found that if these rays are not visible it is because they are absorbed by the media of the eye. It is probable that the rays traverse a great number of substances called opaque. But whether they act directly, or by the intervention of phosphorescent or fluorescent bodies, their effect is still shown by the blackening of the plate on development.

We must here include the effects which spring from an incomplete protection of the sensitive surface during the experiment.

5. It is easy to recognise the X rays on wrapping the plate in black paper, and on placing on the track a thick card or a board with glass and iron, which give a light spot on the black ground due to the rays.

These indications enable us to analyse that which passes in each case, and to analyse the true causes of the phenomena observed.—*Comptes Rendus*, cxxii., p. 598.

A SMALL NOVELTY IN PHOTOGRAPHS WITH THE RÖNTGEN RAYS.

THE photographs obtained with the X rays which have hitherto been published, have doubtless all been produced by the image of the shadow of the transilluminated object upon a sensitive plate, from which copies were thus obtained in the ordinary manner. On transillumination, the parts of the object totally or partially impervious to the X rays produced no impression upon the plate; hence, on the developed plate these parts appeared colourless and transparent, and on the copies black (bones, rings, metallic objects, &c.). The copy also displayed a reflected image of the object taken; hence, *e.g.*, a right-hand appeared as a left, &c. By occasion of a number of experiments which I instituted, Dr. Heseikel suggested that instead of a photographic plate I should use the silver bromide paper which has been introduced into trade. The experiment was very successful. With the silver bromide paper I obtained direct shadow images of the object, the right-hand of the image remained the right-hand, and the portions of the object impervious to the X rays now appeared white, or in the shades of greyish white to grey, which I believe brings out the details better than the former method of operating. The thought suggested itself whether several superimposed silver bromide papers would give simultaneously shadow images of the same object. I placed the superimposed papers and a photo-

graphic plate under a narcotised frog, and illuminated the whole with the X rays. I obtained thirteen shadow images of the same frog without fig. 1 and fig. 13 differing from each other in sharpness or details. In like manner, I have photographed in series the human hand, fishes, and other objects, all with the same result. This new method of operating, besides the advantage that it yields real shadow images of the transilluminated object, is decidedly cheaper, and can be effected in less time than with the circuitous method of the photographic plate. I believe that the medical practitioner who seeks to combine with the photograph surgical operation will be able to make use of this procedure with advantage.

In connection with this subject, Prof. Luntz and I have attempted to ascertain whether X rays are present in the electric arc light. If this were the fact, a sensitive plate placed in a closed case would after development display the shadow image of a piece of metal or a thick glass prism which had been superimposed during the exposure. After exposures of respectively thirty and ninety minutes the result on the sensitive plate was negative.—*Chemiker Zeitung*, February 26, 1896.

ON A NEW AND ABUNDANT SOURCE OF THE RARE OXIDES OF THORIUM, CERIUM, YTTRIUM, LANTHANUM, DIDYMIUM, AND ZIRCONIUM.

By Dr. T. L. PHIPSON.

It has been known for a long time that most of the minerals containing the rare oxides of the metals thorium, cerium, yttrium, lanthanum, didymium, and zirconium are attacked by acids; and I have been able to prove that these minerals, or at least the oxides which characterise them, are more or less widely dispersed through the Norwegian granites. Probably this will be found to be the case with granites from other localities, but my present remarks apply only to the former.

A good many years ago I extracted considerable amounts of zirconium from the zircon-syenite of Norway, of which I brought various specimens to England in 1860, all of which had been seen and verified by the celebrated geologist Dumont, of Liège. In this case, however, the oxide of zirconium was extracted by the usual process, and it served me later (*Comptes Rendus*, 1865) to obtain the metal zirconium by the action of magnesium. I may take this opportunity of stating that M. Moissan has recently been kind enough to point out in the *Comptes Rendus* that this was the first time the metal zirconium had ever been obtained in a state of purity, and he adopted the process in his new researches on that metal.

Being convinced that the rare oxides above named must be widely dispersed throughout the granite rocks of the regions where their minerals are found, I made a number of experiments, not only with the zircon-syenite, but with the ordinary Norwegian granite ("crust" or "tender") which is used along with "Blue Guernsey" and "Aberdeen" for the kerb-stones which pave the road in which is situated my new Casa Mia Laboratory, at Putney. This granite has flesh-coloured and white (or greenish white) felspar, with black mica. The latter, however, becomes quite white after the acid treatment to which I am going to refer.

About 15 to 20 grms. of the rock, reduced to a very fine powder, are heated with pure hydrochloric acid, just as if it were a sample of ironstone. After the acid has been kept gently boiling for about an hour, water is added, and, after depositing, the clear liquid is carefully decanted off through a filter. Another lot of pure acid is then poured over the residue, and it is boiled again in the same manner. A few crystals of chlorate of potash are added to ensure that all the iron is in the state of peroxide. The residue may be digested for two or three days with

strong sulphuric acid, afterwards heated, diluted, and filtered, &c.; but the extra yield of oxides is very small, and the hydrochloric acid treatment alone appears to extract all that is worth having.

The diluted hydrochloric acid liquid is saturated with ammonia until only a very small amount of free hydrochloric acid remains, and then an excess (about a grm.) of crystals of oxalic acid is thrown in and dissolved by stirring. The liquid, having stood for twenty-four hours, is decanted from the precipitate, and the small quantity of free hydrochloric acid is exactly saturated with ammonia; it is then allowed to deposit its oxalates again in presence of an excess of oxalic acid. In this manner the rare oxides are classified into two categories: those whose oxalates resist a little free hydrochloric acid, and those which only resist free oxalic acid.

The oxalates, being dried and calcined, yield a mixture of the rare oxides and carbonates of the metals mentioned above, much cheaper than by employing the expensive minerals thorite, orangite, cerite, gadolinite, monazite, pyrochlor, eudialite, &c., usually required for this purpose. The oxides named have been tolerably well characterised in the products obtained as above; but I can give no idea of their respective quantities more than to say that ceric oxide, yttrium, and didymium, with lanthanum, appear the most prominent, whilst thorium and zirconia were somewhat less abundant. Very slight quantities of some metal (or metals) precipitable by HS (black precipitate in acid liquid) are present also. By the above process I obtained 1·93, or nearly 2 per cent, of rare oxides and carbonates. This yield shows that there are, dispersed through the Norwegian granite (independently of the zircon-syenite), hundreds of tons of the rare oxides which can be promptly and easily extracted, and to some extent separated by the process I have just described.

The calcined oxalates from the liquor containing a little free hydrochloric acid yield a brick-coloured mixture of oxides and carbonates, which contains cerium oxide with zirconia or thorium (or both) amounting to 0·33 per cent; this yields to hydrochloric acid 0·03 of an oxide (yttria or lanthana), giving a very bulky oxalate. The oxalates from the liquor containing only free oxalic acid yield, on calcination, a greenish brown, or brown, mixture of oxides and carbonates, which colour is not due to manganese (which is not precipitated in the above circumstances), and amounting to 1·60 per cent. This product also contains much cerium oxide, with didymium, lanthanum, and yttria.

The Casa Mia Laboratory, Putney.

THE COMPOSITION OF WATER. A SHORT BIBLIOGRAPHY.

By T. C. WARRINGTON, B.A.

(Continued from p. 138).

II. Determination of the Ratio of the Combining Volumes of Hydrogen and Oxygen.

(16). 1805. HUMBOLDT and GAY-LUSSAC.

"Expériences sur les moyens Eudiométriques et sur la Proportion des Principes Constituans de l'Atmosphère."

Jour. de Physique, (1805), lx., p. 129.

Silb. Ann., (1805), xx., pp. 38 and 139. (Translation).

In searching for the best eudiometric means of estimating N and O in air, the authors decide on the use of Volta's method by explosion of the two gases. They find that two volumes of hydrogen explode with one of oxygen to form water.

(17). 1805. CHAPTAL and BERTHOLLET.

"Rapport sur un Mémoire présenté par MM. Humboldt et Gay-Lussac."

Ann. Chim. et Phys., (1805), liii., p. 239.

Resumé of above paper (16), with comments.

(18). 1887. A. SCOTT.

"On the Composition of Water by Volume."

Proc. R. S., (1887), xlii., p. 396.

Chem. News, (1887), lvi., p. 173.

Abs. J. C. S., (1888), liv., p. 411.

Beibl. Wied. Ann. (1887), xi., p. 743.

Both gases are measured in the same vessel, a separate vessel being used for explosion. The residue is analysed.

(19). 1887. A. SCOTT.

"On the Composition of Water by Volume."

Rep. of Brit. Assoc., (1887), p. 668.

Abstract of results of experiments.

(20). 1888. E. W. MORLEY.

"On the Determination of the Atomic Weight of Oxygen." (Dated Nov. 27, 1887).

Amer. Chem. J. (1888), x., p. 21.

Abs. J. C. S., (1888), liv., p. 649.

Beibl. Wied. Ann., (1888), xii., p. 731.

The paper is preliminary and describes the method adopted, part of which consists in the determination of the actual combining volumes of hydrogen and oxygen. No results are given. The method of Scott is criticised (18).

(21). 1888. SYDNEY YOUNG.

"The Composition of Water."

Nature (Feb. 23, 1888), xxxvii., p. 390.

Letter, attempting to establish a relation between the impurity in the gases used and the calculated ratio of volumes in Scott's results, with an attempt to fix the true value of the ratio.

(22). 1888. S. YOUNG.

"The Composition of Water."

Nature (March 1, 1888), xxxvii., p. 416.

Letter, supplementing previous one in the light of Scott's additional results.

(23). 1888. A. SCOTT.

"The Composition of Water by Volume."

Nature (March 8, 1888), xxxvii., p. 439.

Letter, giving some results and a cause of error, viz., use of lubricant.

(24). 1890. E. W. MORLEY.

"Determination of Volumetric Composition of Water." (Abstract).

Proc. Amer. Ass. (1890), xxxix., p. 161.

Nature, (1890), xlii., p. 530.

The method is briefly described and some results are given.

(25). 1891. E. W. MORLEY.

"The Volumetric Composition of Water."

Amer. Jour. Sci., (1891), [3], xli., pp. 220 and 276.

Chem. News, (1891), lxiii., pp. 218, 229, 239.

Abs. J. C. S., (1891), lx., p. 976.

Beibl. Wied. Ann., (1891), xv., p. 679.

Previous work is reviewed with copious references; a new method is described and results are tabulated.

(26). 1891. W. A. R.

"The Composition of Water."

Chem. News, (1891), lxiii., p. 236.

Letter, criticising Morley (24).

(27). 1892. A. LEDUC.

"Application de la Mesure des Densités à la Détermination du Poids Atomique de l'Oxygène." (Note).

Compt. Rend., (1892), cxv., p. 311.

Chem. News, (1892), lxvi., p. 149.

Abs. J. C. S., (1892), lxii., p. 1388.

Beibl. Wied. Ann., (1893), xvii., p. 1.

The author uses his previous determinations of the densities of the gases (11), and determines their relative volumes by electrolysis.

(28). 1893. A. SCOTT.

"On Composition of Water by Volume."

Phil. Trans., (1893), clxxxiv., p. 543.

Proc. R. S., (1893), liii., p. 130. (Abstract).

Abs. J. C. S., (1893), lxiv., II., p. 515.

Chem. News, (1893), lxvii., p. 243.

Beibl. Wied. Ann., (1893), xvii., p. 686.

Zeit. Phys. Chem., (1893), xi., p. 832.

Complete account of author's work.

(To be continued.)

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING FEBRUARY 29TH, 1896.

By WILLIAM CROOKES, F.R.S.,

and

PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, March 10th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from Feb. 1st to Feb. 29th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined one was recorded as "clear but dull," the remainder being clear, bright, and well filtered.

The rainfall at Oxford during the month has been 0.36 inch, as against 1.76 inches, the average for the past 30 years; this shows a deficiency of 1.40 inches, as compared with the average.

The rainfall in the Thames Valley during the months of January and February shows a deficiency of nearly 3 inches on the average of 30 years. This extraordinary dryness has practically reduced the Thames supply to natural springs. As a necessary consequence the unfiltered Thames water shows now quite an exceptional degree of purity. The increase of rainfall, which must in all probability occur soon, will no doubt bring the River back to its normal condition.

During the past month the water supplied to the Metropolis was of first-rate quality.

Our bacteriological examinations for the month of Feb-

ruary resulted in the following numbers of Colonies being found per cubic centimetre :—

	Colonies per c.c.
Thames water, unfiltered	1453
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	46
Ditto ditto lowest	14
Ditto ditto .. (12 samples) mean	26
New River water, unfiltered	1368
New River water, from the Company's clear water well	29
River Lea water, unfiltered	1109
River Lea water from the East London Com- pany's clear water well	28

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 137).

CHAPTER VIII.

THE CHARACTERISTICS GIVEN TO FLAMES, AND TO AN ELECTRIC SPARK, DISCHARGE, OR ARC, BY STRONTIUM COMPOUNDS.

The Luminous Spectra of Strontium.—In this research my object was to ascertain whether a strontium compound could be formed which, when brought to the highest possible temperature in a flame, or an electric spark, discharge, or arc, would not show, on spectrum analysis, conclusive traces of the spectra of sodium, potassium, lithium, calcium, or barium.

To obtain oxide of strontium, I started with purified carbonate, as is described in the preceding chapter. I must warn any one who takes up this subject, that he will have very great difficulty in getting carbonate of strontium completely freed from carbonate of calcium. Besides, the variations found by my illustrious master, Dumas, during his work on the atomic weight of strontium, show conclusively how extremely difficult it is to entirely separate the barium and calcium which are so intimately associated with chloride, nitrate, and carbonate of strontium. The necessity for effecting a complete separation is much greater when, under the conditions mentioned, the flame spectrum of strontium shows the *green lines* which indicate the presence of either calcium or barium in the compound submitted to analysis.

The conversion of carbonate into hydroxide of strontium was performed in the same manner as that of carbonate into oxide of calcium. The decarbonisation, although slower, can be completely effected if care is taken to use an oxyhydrogen blowpipe with an excess of hydrogen, and to heat it with that part of the flame whose temperature is high enough to melt platinum.

By proceeding thus, even although all possible precautions have been taken to protect the very purest carbonate of strontium from atmospheric sodium dust, as soon as it is made red hot the oxyhydrogen blowpipe flame turns *yellow*, and the sodium line appears very strongly when the carbonate has been long in contact with air. Still, by exercising great care and attention, after heating it for a time which varies between fifteen and twenty minutes, and after volatilising at least half the hydroxide produced, the sodium may be so far eliminated that the blowpipe flame will show, on spectrum analysis, only fugitive traces of the sodium line.

I made a great many experiments with the object of ascertaining whether I could see the strontium spectrum

without the sodium line, but I only succeeded *twice*. This happened when I was working in pure air, or rather when spectrum analysis of an oxyhydrogen blowpipe showed no trace of the sodium line, and, in order to preserve the relative purity of the air, I took care the previous evening to effect the decarbonisation, and to eliminate sodium from the hydroxide of strontium I was about to experiment with, and I also had the benches and the floor thoroughly washed at the same time.

I must add that the elimination of sodium so far as to show the sodium line no stronger than it usually appears in an oxyhydrogen blowpipe in air, is a very delicate operation, and that one frequently succeeds only in burning a hole in the concave platinum plate holding the fused hydroxide.

Although there is this difficulty, yet, by putting the hydroxide, as free as possible from sodium, into a conical cup in another concave sheet of recently heated platinum, and by fusing it in a hydrogen blowpipe to get rid of sodium as far as possible, a stage is reached at which a splendid strontium spectrum is seen without a trace of the sodium line, provided that the air at that very moment does not show the latter spectrum; in the other case, the sodium line appears almost as distinctly in the strontium spectrum as in the oxyhydrogen blowpipe. When the air happened to be pure—a state which only occurred twice during the six months occupied by my research on strontium—careful observation enabled me to note variations in the appearance and disappearance of the sodium line.

If, after having freed the outer layers of fused hydroxide of strontium from sodium, in an oxyhydrogen blowpipe, one volatilises it, and so exposes deeper layers, the sodium line reappears, only to disappear once more. I succeeded one day in causing these alternations, which gradually lessened in intensity, when volatilising several grms. of pure hydroxide of strontium in an oxy-coal-gas blowpipe.

This hydroxide freed from sodium, when left for twelve hours in air under a bell jar, and then introduced into an oxyhydrogen blowpipe, showed the sodium spectrum in just the same way as platinum, silver, oxide of lithium, and oxide of calcium, which had been in contact with air.

The flame of an oxyhydrogen blowpipe assumed a *deep purplish red* colour when projected on to pure fused hydroxide. At a temperature near the fusing-point of iridium, the purple colour was replaced by a *deeper blue* than that of incandescent hydrogen.

For instance, on introducing hydroxide into the *inner cone* of an oxyhydrogen blowpipe, by means of a small cone of pure carbon, the point of contact becomes *deep blue*, and the rest of the flame a *purplish colour*.

Fused hydroxide, and more especially its vapour, attacks platinum, colouring it black. Its vapour makes air pungent, but less so than the vapour of oxide of calcium. When left undisturbed, strontium settles in air more rapidly than calcium and lithium. Although I have frequently made heavy fumes of oxide of strontium, after three or four hours, I was unable to detect the least trace of a strontium spectrum in an oxyhydrogen blowpipe. After calcium and lithium had been freely volatilised,—as I had to do during my researches,—the air had to be left undisturbed for at least eighteen hours before an air spectrum could be shown without disclosing their presence. Oxide of lithium is so volatile that, several hours after I finished my work, burners in the next room to the one I was working in still showed a very distinct lithium colour.

The Flame Spectrum of Strontium.—In his remarkable work on spectrum analysis, Roscoe gives such a correct illustration of the spectrum of chloride of strontium, as measured by Messrs. Bunsen and Kirchhoff, that no description can improve upon it. When seen in a hydrogen or coal-gas flame, the spectrum consists of six red bands, one orange band, clearly separated if the slit is narrow enough, on a dark background, and *one* blue line.

Oxide or hydroxide of strontium, when introduced into an oxyhydrogen or oxy-coal-gas blowpipe, at a temper-

ature below the fusing-point of platinum, forms a spectrum like that described above. But on making a spectrum analysis of a blowpipe flame heated up to the fusing-point of platinum, and making the slit sufficiently narrow, the six red bands and the orange band are resolved into *diffuse* and *nebulous* lines; that is to say, they lack the sharpness of the blue line, and more especially of the lines formed by means of an electric spark charged with anhydrous chloride or hydrate of strontium. The spectra of the sharp bands are always similar.

It is possible to completely volatilise pure oxide or hydroxide of strontium in an oxyhydrogen or oxy-coal-gas blowpipe, without seeing any other lines on the dark background, by taking care to analyse only that part of the strontium flame in which the hydrogen is not incandescent, and which above all does not show a continuous spectrum.

When a part nearer to the inner cone, and most especially the inner cone itself, of a flame charged with strontium is analysed, the spectrum becomes modified; there are then seen, with oxyhydrogen gas, a dark band from A nearly to D, marked by the seven red bands and a strong, diffuse, orange line, and a green tinge from D to F. This tinge shows *three*, and sometimes *four*, green lines. The same thing is seen when using an oxy-coal-gas blowpipe. The colour of these green lines is quite distinct from that of either calcium or barium lines, and is the same as that of the green lines in the spectrum of the inner luminous cone of oxy-coal-gas itself, as I described in the first chapter.*

However much I tried to see the two violet-blue lines observed by M. Bunsen at 136.5 and 150.5 on his spectroscopic in the spark spectrum of chloride, I could not find them. I found, on the other hand, that the introduction of hydroxide of strontium into the inner luminous cone of an oxy-coal-gas blowpipe immediately showed the two blue bands and the blue line shown by spectrum analysis of this oxy-coal-gas cone. In this case the spectrum consisted of six diffuse red lines and a very strong orange line, on a dark background and characteristic of strontium, of two green bands on a luminous background, consisting of three and sometimes four sharp lines fading off from left to right, and finally of the blue strontium line on a dark background.

In order to find out, on the one hand, whether the green lines seen really belong to the flame spectrum of hydroxide of strontium, and, on the other hand, whether the absence of the two new violet-blue lines at 136.5 and 150.5, seen by M. Bunsen in the spark spectrum, are due to my method of investigation,—that is, to the oxyhydrogen blowpipe,—or to a difference in the compound, I examined the spectrum of chloride of strontium both in an oxyhydrogen and in an oxy-coal-gas blowpipe, and also in an electric spark, discharge, and arc.

An oxyhydrogen blowpipe in which the hydrogen is not incandescent, when impinged on to chloride of strontium, shows, on spectrum analysis, the same spectrum as that seen with hydrogen or a Bunsen lamp burning in air. On sufficiently closing the slit, the bands become nebulous lines. The bands and lines appear to undulate in the same way as those due to chloride of calcium heated in the same way. This apparent undulation lasts until the chloride is completely dissociated.

Anhydrous chloride of strontium, when put, by means of a small cone of pure carbon, into that part of an oxyhydrogen blowpipe where rhodium and iridium are fused, forms a flame *white in the centre, blue in the middle, and deep red round the edge*, in which spectrum analysis shows the six red bands almost merged into one. These bands only appear as nebulous lines after the chloride is dissociated and transformed into hydroxide or oxychloride of strontium.

At the same time that the red bands are seen merged together, there are also visible the strong orange line quite distinct, and *three or four* green lines fading off from

right to left, and a single blue line. Every attempt to cause TO APPEAR, or at least TO SEE, at the same time the two pale violet-blue lines, seen by M. Bunsen in the electric spectrum, failed.

I got a different result when analysing a spark or a discharge from an induction-coil, with or without a condenser, charged with chloride, or with the hydroxide formed by dissociating chloride. For these researches I used in succession a Steinheil spectroscope, a large instrument by M. Hilger, fitted alternately with three or six prisms of Iceland spar, a spectroscopic with two half-prisms of quartz, made by M. Hilger for M. Depaire, and a direct-vision spectroscopic that Messrs. Liveing and Dewar kindly had made for me by M. Hilger.

During my observations, I used at first platinum balls and then small cones of pure carbon, coated either with chloride, oxychloride, or hydroxide of strontium. These compounds, when volatilised in an induction-spark or discharge, imparted a deep blue colour to them, and showed long and complete lines on spectrum analysis. Having found that the number and brightness of the air lines varied with the space between the coated balls, I replaced them by pure platinum balls fixed at half a c.m. apart, using coils which gave sparks of five, fifteen, and forty-five c.m. length.

After having found that, with this invariable distance, the number and position of the air lines were constant, I wetted the balls by means of a fine platinum wire loop, coated with a fluid paste of crystallised and dissolved chloride of strontium, quite free from calcium and barium, or I simply coated them with a saturated solution of hydroxide of strontium made from chloride or carbonate dissociated in an oxyhydrogen blowpipe. I thus found that, after deducting the air lines, the spectrum of a weak or strong induction spark and of a discharge, charged with chloride or hydroxide, was the same as the spectrum of chloride in a spark as described by Bunsen in Table VI., No. 8, of his "Spectral Analytische Untersuchungen," including in it the last two pale violet-blue lines, tabulated at 136.5 and 150.25 divisions on his spectroscopic, corresponding to 126.5 and 138.5 on my Steinheil spectroscopic.

Spectrum analysis of the discharge from a Ruhmkorff coil, giving sparks 45 c.m. long, between platinum balls or pure carbon cones coated with chloride or hydroxide of strontium, or the same balls or cones wetted with a saturated solution of these compounds, showed, together with the numerous and inevitable air lines, exactly the same lines that were seen with a spark, either weak or strong.

These investigations have convinced me that there is no advantage in increasing the electrical power of a spark. As far as the number of lines is concerned, there is no difference between the spectrum of chloride or hydroxide of strontium with a five, fifteen, or forty-five c.m. spark, when they are reduced to a half c.m. by moving the coated balls or cones nearer together. But the luminosity and colour of the lines, and more especially their visibility, increase with the electric power. The strontium spectrum does not alter after the characteristic strontium lines in a spark have appeared, and the difficulty of observing and fatigue of the eyes are accentuated by the appearance of a greater number of air lines.

In an electric arc formed by thirty of the largest-sized Bunsen cells, between pure carbon electrodes in contact and coated with fused chloride or hydroxide, the same lines are visible as those seen in the discharge, but with this difference—that in the arc spectrum of strontium these air lines, which make an examination of the discharge spectrum so difficult and fatiguing, do not appear.

Bunsen found the following bands and lines to be common to the flame and electric spectra:—

Flame Spectrum.		Electric Spectrum.	
Bunsen.	Stas.	Bunsen.	Stas.
36 to 37	37 to 38	36 to 37	36 to 38
39	40	39	40
47	47	47	47
105.5	98.5	105.5	98.5

* See CHEMICAL NEWS, vol. lxxii., p. 226.

I found the same bands and lines to be common to both spectra. I found besides that, beyond the fusing-point of platinum, hydroxide from carbonate and chloride of strontium has, in its flame spectrum, three, and sometimes four, green lines *common to the spectrum of chloride and hydroxide* in the spark and arc. These green lines are quite absent from the flame spectrum when the hydrogen is not incandescent.

The *strong* band in the flame spectrum between 31 and 34 on Bunsen's spectroscopic scale, only appeared in my research in a rudimentary form in the electric spectrum, however intense the spark or arc might be, and, on the other hand, I was unable to cause in an oxyhydrogen spectrum the appearance of the line at 89.75, mentioned by Bunsen in the spark spectrum, and frequently seen by myself in the same spectrum, both with chloride and hydroxide of strontium at 85 divisions on my Steinheil spectroscopic scale.

The flame spectrum of strontium varies with the temperature. Its appearance is different in hydrogen burning in air and in hydrogen highly incandescent. Both these spectra are typical, but can be changed from one to the other by altering the temperature.

I utterly failed to find either of them in the electric spectrum. The flame spectrum, whether complete or incomplete, preserved its characteristic appearance, whatever I did. Certain of its bands, perhaps, might be resolved almost into lines, but the edges of these lines remained diffuse; the orange band persisted longest.

The electric spectrum of chloride and hydroxide of strontium has some lines in common with the flame spectrum of the same bodies. This spectrum cannot be changed into either of the flame spectra of strontium.

My researches tend to prove the existence of three distinct types of strontium spectra. The second type of flame spectrum appears to be a step towards the spark and arc spectrum; but I was not able to make the change. Until the contrary is proved, I must consider the flame and electric spectra of strontium to be different.

I was unable to obtain chloride of strontium which showed no trace of the sodium line when introduced into a spark; but the hydroxide made by its dissociation, when put, as soon as it was made, into an electric spark or arc, showed a spectrum in which the sodium line was no stronger than it was in a spark or arc passing in the air.

When revising my spectroscopic research on chloride and hydroxide of strontium, in collaboration with M. Depaire, we undoubtedly found that, on analysing the rays from the inner cone of an oxy-coal-gas blowpipe saturated with chloride or hydroxide of strontium, we could see neither the *second* nor the *third* violet-blue line discovered by Bunsen in the electric spectrum, and this when using a spectroscopic scale which showed both these lines in a spark or arc saturated with chloride of strontium.

We ascertained definitely that the electric spectrum of strontium was unchangeable, by submitting the chloride and hydroxide of this metal to the same currents that we used for studying the arc spectrum of lithium and calcium, and using the same spectroscopes. In other words, we used a current made by the battery of thirty-three Julien accumulator cells, and a current from the Gramme and Siemens dynamos *coupled*, attaching carbon electrodes to the Gerard regulator.

We thus found that spectrum analysis of the strong light produced by the contact of the electrodes showed a spectrum, consisting of a continuous spectrum, on which was superposed that of strontium, and that analysis of the arc showed a continuous spectrum, on which was superposed both the strontium spectrum and the lines of the electric spectrum of carbon.

In both cases, the spectrum of strontium was the same as that illustrated by Bunsen in his work on the electric spectrum of chloride of strontium.

The diffused lines seen in the spark spectrum, with or without a condenser, remain diffused in an arc, however

powerful, though to a less degree. At the instant the chloride of strontium is introduced into the arc, the sodium line becomes visible. This line rapidly decreases in intensity, and, long before the bulk of the chloride is volatilised, the sodium line is no stronger than it is in an arc passing in air between electrodes free from strontium. It may therefore be said that there is no connection between the sodium spectrum and the electric spectrum of strontium.

It follows from the above that the flame and electric spectra of strontium have no connection with the luminous spectra of potassium, lithium, and calcium, and that the electric spectrum of strontium is unchangeable in the conditions under which my researches were carried on.

(To be continued).

THE EAST LONDON TRADES INDUSTRIES AND ARTS EXHIBITION,

AND

GENERAL EXHIBITION OF THE WORK OF STUDENTS
IN POLYTECHNICS AND TECHNICAL INSTITUTES.

WE have great pleasure in referring to this Exhibition, which is to take place in June. Every movement which can induce the people of the East End to seek elevation as individuals and a class, by the advance of the arts and industries in which they are engaged, deserves the warmest support. Our progress as a nation would, however, be much brightened if we could be induced to abandon our delusive system of examinationism. We have just seen its failure on a magnificent scale in the recent collapse of China, the country where competitive examination was first devised, and, after being carried out for centuries, has proved ruinous alike morally and intellectually. Shall we take this lesson to heart?

The departments of the forthcoming Exhibition are announced as a special section for the work of individual craftsmen; secondly, a section for the work of apprentices and of students at the London Polytechnics; and thirdly, a women's section. Unfortunately these sections have relatively little connection with the industries and arts in which we feel the greatest interest.

The technical training of students is of the greater importance, since it is not so much the rank and file of our industrial army, as its leaders,—managers, overlookers, foremen, and even the heads of establishments,—who are not fully on a par with their rivals in Germany, Switzerland, and Belgium.

We are doubtful as to the policy of introducing concerts and other entertainments in connection with an industrial exhibition. Amusements seem to be coming too much to the front, not merely at the People's Palace, but at the Imperial Institute and at certain so-called Aquariums.

We hope that ample funds may be secured for the projected Exhibition, and that they may be expended in promoting the technical prosperity of East London—hence of the Empire at large.

Molybdic Acid as a Reagent for Alcohol.—E. Merck.—The author finds, on experiment, that even minimum traces of alcohol can be detected in aqueous solutions by his special molybdic acid (Acidum molybdenic, pur.). The sensitiveness of this test extends for ethylic alcohol to 0.02 per cent, and for methyl alcohol to 0.2 per cent. Molybdic acid is dissolved in concentrated sulphuric acid, and the solution thus obtained is stratified in a test-glass at about 60° below the liquid under examination. At the surface of contact of the two liquids there appears a distinct blue ring, the more intense in colour the larger the proportion of alcohol. On shaking the blue zone disappears, but reappears on the addition of more molybdic acid. The reaction is not specific for alcohol.—*Chemiker Zeitung*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 5th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 140).

*32. "Note on the Use of Certain Phosphorescent Substances in rendering X Rays Visible." By HERBERT JACKSON.

In a former paper, on "Observations on the Nature of Phosphorescence" (*Trans.*, 1894, 734), the author drew attention to the similar nature of the phenomena of phosphorescence obtained with various substances placed either inside or outside of a vacuum tube.

Since the publication of that paper the work has been continued, mainly with a view to studying the relation of phosphorescence to the chemical structure, and more especially to the spectra of the substances which exhibit the phenomena. The present note is put forward because the author's experience has enabled him to obtain useful results in the attempt to render certain structures, &c., visible by means of the radiations, the effect of which on photographic plates has latterly attracted so much attention.

The existence of something proceeding from a vacuum tube capable of penetrating many otherwise opaque bodies was first made public by Lenard. The author employed at the time, and has since used, such substances as ebonite, metals, and other opaque sheets, as windows or covers to vacuum tubes in studying phosphorescence with such receptive substances as the platinicyanides, the oxides and carbonates of many metals, and the sodium, potassium, and lithium haloids.

The knowledge of the nature of the radiations which induce phosphorescence in many substances outside a vacuum tube has recently been very greatly added to by Professor Röntgen's discovery that they exhibit none of the phenomena of refraction, diffraction, and interference. To this important discovery he has added the interesting observation of the relative transparencies of bone and flesh.

The vacuum tube most suitable for showing the phenomena, in the writer's experience, is a slight modification only of one invented by Mr. Crookes to illustrate the heating effect of focussed radiant matter.

It consists of a concave aluminium cathode and a platinum anode. The latter is inclined at an angle of 45° , and spreads the rays from the cathode in every possible direction, apparently by scattered reflection.

Such a tube has been regularly employed by the author in experiments upon the phosphorescence of the platinicyanides, and of some three hundred other substances, and was first used by him in January, 1894. About seventy tubes were made in the attempt to obtain the best results, but so far the one described has proved to be the most active.

To obtain good results the vacuum must be high. Apparently the nature of the residual gas does not affect the working of the tube in any marked manner. Both Dr. Norman Collie and the author have tried a number of gases without noticing any marked difference. This may be largely due to the fact that if a mercury pump be used a very considerable percentage of the residual gas is the vapour of that metal.

The most brilliantly phosphorescent substance yet obtained is potassium platinicyanide. This salt crystallises with three molecular proportions of water, and is most active in its fully hydrated state. It effloresces, and should therefore be used in such a way that either it cannot lose water or can be readily moistened. If this platinicyanide be painted on to black cardboard, or thin

vulcanite, &c., its phosphorescence will enable transparent and opaque objects to be clearly differentiated.

The particular potassium salt was chosen from considerations of the brilliant expanse of blue seen in the spectrum of compounds of that metal. Many of the other platinicyanides have been tried, as well as a number of the platamine salts. With none of them is the amount of light equal to that of the potassium salt.

A study of the phenomena during the exhaustion of the tube shows that the rays (it is convenient to speak of rays) proceeding from the concave cathode meet apparently at the centre of curvature and diverge in a solid cone. As the vacuum becomes higher this cone narrows until, when the exhaustion required for the maximum phosphorescence outside the tube is attained, it apparently becomes a straight line.

If, as at present observation seems to indicate, the rays from the cathode are still brought to a focus at the centre of curvature, the fact that they proceed thence in a straight line gives a material aspect to the phenomenon, as this would be the behaviour of particles coming at right angles from the surface of a concave disc, and colliding at the centre of curvature. This, however, would require the assumption that the particles are non-elastic. It is possible that only the centre of the electrode is implicated at high exhaustions. The author is conducting experiments with a view to settle this question of the path of the rays. It does not seem probable that the radiation is confined to the centre, because a straight cathode gives none of the effects observed when the concave form is used. When the rays meet the reflecting platinum plate, which is conveniently, but not necessarily, made the anode, they are scattered by the relatively coarse surface of the metal, a very small circle upon which becomes the radiant. This is shown by experiments with phosphorescent substances placed upon the platinum, and by examining the tube through a pin-hole in an opaque metal sheet by means of a phosphorescent screen. The results obtained are only consistent with the source of illumination being a point or a very small circle. The alternative to the view that the cathode is the true original source of the exciting cause, and that the rays proceed from the glass, is disproved by using flat and curved tubes. A point as the illuminative source would be obtained if rays proceeded at right angles from the surface of a curved glass, but not from a flat one.

In his previous paper the author attempted to show that all the phenomena of phosphorescence, either inside or outside a vacuum tube, were best explained on the assumption that the exciting cause proceeding from the cathode was of the nature of light, or was capable of setting into vibration the residual gas particles so as to give rise to undulations of the nature of light. Professor Röntgen has expressed an opinion in favour of longitudinal vibrations. The author adheres at present to the notion of transverse vibrations, and hopes before long to bring further experimental evidence before the Society in dealing with his work on the relation of the spectra of substances to their phosphorescence.

DISCUSSION.

Sir JOSEPH LISTER remarked on the probable importance to medicine and surgery of the discovery that the shadows produced by the Röntgen rays could be rendered visible to the naked eye in the manner which had been demonstrated by Mr. Jackson.

Dr. ARMSTRONG thought it would be found, when Mr. Jackson's full communication was studied, that he had not only materially advanced the application of Röntgen's most remarkable discovery, but also added much to our knowledge of the phenomena concerned. His success was due to no chance observations, but was the outcome of prolonged, thoroughly scientific study of phosphorescent phenomena, and a development of his previous work.

It was certainly very startling to see, with the aid of a

mere screen held before the eyes, the bones in the foot right through the boot, and to learn that a photograph could be secured in the merest fraction of a second with the aid of such a screen. He believed that Mr. Jackson was of opinion that there were a great variety of Röntgen radiations, and that different objects were opaque to these in different degrees; so that it might ere long be possible, by properly selecting the radiations, to distinguish objects much more closely related than bones and flesh.

*33. "The Union of Carbon and Hydrogen." By WILLIAM A. BONE, M.Sc., Ph.D., and DAVID S. JORDAN, M.A., B.Sc.

Two years ago one of the authors, in conjunction with J. C. Cain (*Proc. Chem. Soc.*, 1894, 56), observed that when a mixture of cyanogen and hydrogen is fired in a long lead coil with a volume of oxygen insufficient to burn all the carbon present to carbon monoxide, a small amount of methane, varying from 1.0 to 1.7 per cent, according to the composition of the original mixture, was found among the products of explosion. This seemed to indicate the possibility of the formation of methane by the union of its elements at the high temperature of the explosion wave, and the authors undertook the following experiments, with a view of testing this hypothesis. They have investigated (1) the effect of heating carefully purified carbon (obtained by heating sugar charcoal in chlorine and subsequently in hydrogen until all the chlorine was expelled) in a glazed Berlin porcelain tube to white heat, in an atmosphere of dry hydrogen free from hydrocarbons; and (2) the action of carbon upon hydrogen at the temperature of the electric arc.

In the first series of experiments the porcelain tube was heated in a Fletcher injector furnace by means of an air-coal-gas blowpipe. In order to avoid the possibility of the diffusion of furnace gases through the porcelain tube, it was placed inside a wider tube of the same material, and a current of hydrogen was passed through the annular space between them. Several blank experiments were performed, in which hydrogen free from hydrocarbons was passed through the inner tube and through the jacket, whilst the tubes were maintained at a white heat; samples of hydrogen taken from the inner tube during the course of an experiment were found, on analysis, to contain no carbon compound. The purified carbon, after being dried over phosphoric anhydride for two months, was strongly heated in a hard glass tube attached to a Sprengel air-pump, and was then sealed up in a vacuum with quick-lime. This carbon was introduced into the inner porcelain tube, and was heated to white heat in a current of hydrogen free from hydrocarbons, whilst simultaneously a current of the same hydrogen was passed through the space between the inner and outer tubes. Samples of the exit gases from the inner tube were afterwards carefully analysed; they were found to contain no acetylene or other unsaturated hydrocarbon, but about 1 per cent of methane. In another experiment, a volume

of hydrogen was enclosed in the inner tube, heated for three hours in contact with the carbon; on subsequently analysing the gas, it was found to contain nearly 2 per cent of methane.

In the second series of experiments, the electric arc was formed between terminals of purified gas-carbon in an atmosphere of dry hydrogen free from hydrocarbons, contained in a glass globe standing in a trough over mercury. Each of the carbon terminals, which had been previously strongly heated for several hours in a hard glass tube connected with a Sprengel air-pump, was attached to a stout copper wire, which in turn was fixed into a piece of narrow glass tubing bent into U shape and filled with mercury. The limb of the U-tube bearing the carbon was then thrust into the globe from below the surface of the mercury in the trough. The top of the globe was drawn out and sealed to a three-way tap, by means of which connections could be made, on the one hand, with an air-pump for the supply of hydrogen, and, on the other hand, to a nitrometer full of mercury, which served to collect samples of the gas in the globe at intervals during an experiment.

At the outset of an experiment, the globe was exhausted of air by attaching it to a working air-pump until it was completely filled with mercury. Then dry hydrogen was introduced, and the arc passed between the terminals for about a quarter of an hour. The globe was again exhausted, and finally filled with the dry purified hydrogen. The arc was then passed for a period of time varying from thirty minutes in the first experiment to two hours in the last, and at the end of five, fifteen, thirty, &c., minutes in each experiment, samples of the gas were drawn off for analysis.

Composition of the Gases.—The gases were always found to contain small amounts of hydrocyanic acid, due no doubt to the presence of a little nitrogen in the hydrogen employed. Acetylene was also present in considerable quantity, and was detected by passing the gas through an ammoniacal solution of silver chloride, when a copious precipitate of silver acetylide was formed. A detailed analysis of the gases showed, however, that, in addition to acetylene or other unsaturated hydrocarbon, they invariably contained an appreciable amount of some saturated hydrocarbon, most probably methane.

The gases were analysed in a modified form of the McLeod apparatus. A large volume of the gas was successively treated with solid potash, fuming sulphuric acid, acid solution of cuprous chloride, and a dilute solution of potash, in order that all hydrocyanic acid, unsaturated hydrocarbon, and any traces of carbonic oxide might be removed; a portion of the residual gas was then exploded with excess of air, free from carbon dioxide, and the contraction and absorption by potash solution after the explosion determined. Finally, the excess of oxygen was absorbed by means of alkaline pyrogallate, and the residual nitrogen measured.

The results of the analyses are tabulated in percentages.

Experiment.	Gases drawn off after	Minutes.						
		5.	15.	30.	45.	60.	90.	120.
A ..	Absorption by solid potash [hydrocyanic acid] ..	0.20	1.01	1.51	—	—	—	—
	Absorption by fuming sulphuric acid and cuprous chloride solution, <i>i.e.</i> , ethylene, acetylene ..	5.10	8.43	9.85	—	—	—	—
	Methane	1.32	2.20	2.46	—	—	—	—
B ..	Absorption by solid potash [hydrocyanic acid] ..	0.11	0.20	0.12	0.20	—	—	—
	Absorption by fuming sulphuric acid and cuprous chloride solution, <i>i.e.</i> , ethylene, acetylene ..	2.13	4.99	6.41	8.08	—	—	—
	Methane	0.64	1.38	2.26	2.26	—	—	—
C ..	Absorption by solid potash [hydrocyanic acid] ..	trace	trace	0.10	—	0.53	1.00	0.39
	Absorption by fuming sulphuric acid and cuprous chloride, <i>i.e.</i> , ethylene, acetylene	2.12	4.70	6.16	—	6.83	6.42	7.59
	Methane	1.00	1.63	2.37	—	2.71	2.15	2.62

In all three experiments an alternating current from a dynamo was used. In Experiment A, the voltage was 160, and in B and C between 40 and 60, but it was extremely difficult to maintain a constant voltage throughout a long experiment.

34. "Note on the $\alpha\alpha$ -Dimethylglutaric Acids." By WILLIAM A. BONE, M.Sc., Ph.D., and W. H. PERKIN, Jun., F.R.S.

The authors are now able to confirm the observation of Thorpe and Auwers (*Ber.*, xxviii., 623) that the acid melting at 105–107° which they described in a paper published last year (*Trans.*, 1895, 416), is really an equimolecular mixture of trans- and cis-dimethylglutaric acids melting at 140–141° and 127° respectively. This equimolecular mixture, which in many respects behaves like a homogeneous substance, having, for example, a fairly sharp and constant melting-point, may be resolved into its constituent acids by careful treatment with acetyl chloride, when the cis-acid yields an anhydride, whilst the trans-acid is unchanged, or by fractional precipitation of the acid calcium salts, that of the trans-acid being least soluble.

35. "The Symmetrical Dimethylsuccinic Acids." By WILLIAM A. BONE, M.Sc., Ph.D., and W. H. PERKIN, Jun., F.R.S.

During the course of their investigations on trimethylsuccinic and $\alpha\alpha$ -dimethylglutaric acids last year, the authors obtained a considerable quantity of ethylic dimethylcyanosuccinate as a by-product of the action of potassium cyanide on ethylic α -bromopropionate in alcoholic solution (*Trans.*, 1895, 416). On hydrolysing this ethereal salt by means of concentrated hydrochloric acid they obtained a mixture of trans- and cis-dimethylsuccinic acids, which they were able to separate either by fractional crystallisation from water or by a fractional precipitation of their calcium salts. After studying the literature of the subject, the authors found that the properties of the dimethylsuccinic acids which they had obtained differed considerably from those assigned to them by previous investigators, and they therefore submitted these acids and their anhydrides to a careful examination.

They also prepared the dimethylsuccinic acids by the action of ethylic α -bromopropionate on the sodium compound of ethylic methylmalonate, subsequent hydrolysis of the resulting ethereal salt by means of alcoholic potash, and then heating the tribasic acid so obtained to 200° until all evolution of carbonic anhydride had ceased. The resulting acids were in all respects identical with those obtained by the first method.

Trans-dimethylsuccinic acid when pure melts at 209°, and is very much less soluble in water than the cis-acid, which melts at 129°. The calcium salt of the trans-acid is, however, much more soluble in water than that of the cis-acid. Each acid, when treated with acetyl chloride or acetic anhydride, yields its own anhydride, a fact first observed by Otto and Rössing (*Ber.*, xx., 2736) and confirmed by Bischoff; the trans-anhydride melts at 43° (not 38° as given by Bischoff) and is less stable than the cis-anhydride, which melts at 88°, and is completely transformed into the last-named substance on prolonged heating with acetic anhydride. Both acids, on distillation at atmospheric pressure, yield the cis-anhydride. Each anhydride dissolves in hot water, yielding its own acid, not, as some authorities have stated, a mixture of the cis- and trans-acids.

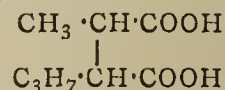
36. "The Cis- and Trans-methylisopropylsuccinic Acids." By WILLIAM HENRY BENTLEY, WILLIAM HENRY PERKIN, Jun., and JOCELYN F. THORPE.

The authors have studied the action of ethylic α -bromoisovalerate on the sodium compound of ethylic methylmalonate in alcoholic and in xylene solution, and find that in both cases the product of the reaction consists of ethylic isopropylmethylethanetricarboxylate,—

$\text{COOC}_2\text{H}_5 \cdot \text{CH}(\text{C}_3\text{H}_7) \cdot \text{C}(\text{CH}_3) \cdot (\text{COOC}_2\text{H}_5)_2$,
a colourless oil, which boils at 200–209° (80 m.m.).

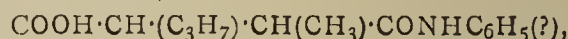
This oil, on hydrolysis and subsequent elimination of carbon dioxide, yields a mixture of cis- and trans-methylisopropylsuccinic acids, which are separated by methods described in detail in the paper.

Cis-methylisopropylsuccinic acid,—

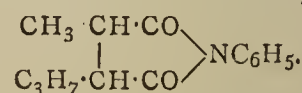


melts at 125–126°, and, when heated with hydrochloric acid at 180°, is partially converted into the trans-modification; when distilled or digested with acetic anhydride, it yields a liquid anhydride boiling at 138–140° (35 m.m.).

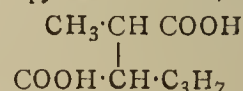
The anilic acid,—



melts at 153°, and, at a somewhat higher temperature, loses water with formation of the corresponding anil,—



Trans-methylisopropylsuccinic acid,—



melts at 174–175°, and is much less soluble in water than the cis-acid; when distilled under diminished pressure, or when digested with acetic anhydride, it is converted into a solid anhydride melting at 46°; and this, when repeatedly distilled at ordinary pressures, is converted into the anhydride of the cis-acid.

The anilic acid obtained from trans-anhydride by treatment with aniline melts at 160°, and a few degrees above this temperature loses water and is converted into the anil of the cis-acid.

The authors have also prepared the methylisopropylsuccinic acids from ethylic isopropylethanetricarboxylate, which Roser (*Annalen*, ccxx., 272) first synthesised by the action of ethylic α -bromoisovalerate on the sodium derivative of ethylic malonate. When this ethereal salt is acted on with sodium ethoxide and methylic iodide, ethylic methylisopropylethanetricarboxylate is produced, and from this ethereal salt the methylisopropylsuccinic acids may be obtained by the method described above.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 9, March 2, 1896.

Observations on Photography through Opaque Substances.—A. d'Arsonval.—Already inserted.

On Invisible Radiations Emitted by Phosphorescent Bodies.—Henri Becquerel.—Will be inserted in full.

Reply to the Observations of H. Poincaré on the Theory of Kathodic Rays.—G. Jaumann.—A purely mathematical paper, not suitable for abstraction.

Observations on the Foregoing Memoir.—H. Poincaré.—The author explains his use of the term "ray."

Exhibition of Proofs obtained by Röntgen's Method.

Dark Light: a Reply to certain Criticisms.—Gustave Le Bon.—Already inserted.

Diffusion of the Röntgen Rays.—A. Imbert and H. Bertin-Sans.—This paper will be inserted in full.

The Photographic Representation of the Relief of a Medal obtained by means of the Röntgen Rays.—J. Carpentier.—Will be inserted in an early number.

Passage of Röntgen's Rays through Liquids.—MM. Bleunard and Labesse.—Already inserted.

Discovery and Extraction by means of a Röntgen Photograph of a Needle embedded in the Human Hand.—Pierre Dalbet.—An instance of the successful application of Röntgen's rays in surgery.

Applications of Röntgen's Method.—Ch. Girard and F. Bordas.—Five detections of enclosed objects.

Extraction of Rhodinol from the Essence of Pelargonium and from the Essence of Roses.—Ph. Barbier and L. Bouveault.—The authors have established the identity of these two essences by a study of their chemical properties and the identification of their derivatives. The proportion of rhodinol is small in each case, not exceeding 20 per cent.

Preparation of Silicichloroform, Silicibromoform, and some Derivatives of Triphenyl-silicoprotane.—Charles Combes.—The author will show in a future paper how he has effected his purpose by employing a tertiary amine.

Oxidation of Crotonic Aldehyd.—E. Charon.—Not suitable for abstraction.

Journal für Praktische Chemie,
New Series, Vol. li., Part 12.

On Phenomena of Isomerisation in the Series of the Carbonyl Compounds of Chlorised Alcohols and Haloid-substituted Oxides of the Ethylenhydrocarbons.—Al. Faworsky.—In this voluminous memoir the author expounds the action of hypochlorous acid upon bi-substituted acetylenhydrocarbons.

Syntheses of Quinazolin Compounds.—St. von Niementowski.—The author describes the synthesis of δ -oxyquinazolin, of δ -oxymeta-toluquinazolin, of β -methyl- δ -oxyquinazolin, of β -methyl- δ -oxymeta-toluquinazolin, of β -ethyl- δ -oxyquinazolin, of β -ethyl- δ -oxymeta-toluquinazolin, of progonmeta-toluid, of β -isopropyl- δ -oxyquinazolin, of β -isopropyl δ -oxymeta-toluquinazolin, and of isobutylra-meta-toluid.

Synthesis of Antipyrin, a Reply to F. Stolz.—R. von Rothenburg.

Cases of Isomerism in the Pyrazol Series, a Reply to L. Kron.—R. von Rothenburg.

On Chemical Equivalence.—R. von Rothenburg.

On the Phthalein-melt.—R. von Rothenburg.

These four strongly controversial papers have already reached the stage which our German colleagues aptly term "unerquicklich," and are passing on into the region of personalities.

Constitution of the Diazo-benzene Compounds.—R. Walther.—A criticism of the results of Meldola and Streatfield.

On the Most Recent Views of Herr Hantzsch on the Diazo-compounds.—Eug. Bamberger.—A criticism of the views of Hantzsch on the constitution of the diazo-compounds.

The Production of Pinakones by the Reduction of Aromatic Ketones.—K. Cebo and K. Schmitz.—The regularity established by the experiments of the authors affords the means of demonstrating, by a simple reduction with zinc-powder and glacial acetic acid, whether a ketone contains its carboxyl group in direct combination with an aromatic group or not.

Parts 13 and 14.

Researches from the Laboratory of the University of Freiburg, in Breisgau.—These researches comprise a paper by Ad. Claus and Alex. Seelemann, on the

sulphonic acids of isoquinolin, and a memoir on isoquinolin by Ad. Claus and C. Gutzeit.

Synthetic Researches in the Pyrazol Series. Parts II. and III.—R. von Rothenburg.

Calorimetric Researches.—F. Stohmann and Raym. Schmidt.—This paper discusses the thermic value of the amides and anilides of monobasic acids.

The Solubility in Water of Certain Substitution Derivatives of Benzene.—W. Vaubel.—The author does not accept the rule proposed by Carnelley and A. Thomson, that for one group of isomeric organic compounds the series of solubilities is at the same time the series of the melting-points,—i. e., the most soluble substance is also the most fusible. There occur a number of exceptions, especially among the kresols, nitrophenols, nitro- and oxybenzoic acids, and probably among the toluidines and nitro-anilines.

Remark on the Memoir of Fileti and Ponzio on the Transformation of the Ketones into α -Diketones.—L. Claisen.—The author accepts the accuracy of the conclusion of Fileti and Ponzio, but protests against their having regarded his former opinion as ultimate.

Reply to the Memoir of R. von Rothenburg on the Constitution of the n -Phenyl-pyrazolones.—L. Claisen.—The author considers any further discussion with C. von Rothenburg as useless.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxiii., No. 1.

This issue contains no chemical matter.

MEETINGS FOR THE WEEK.

TUESDAY, 31st.—Institute of Civil Engineers, 8.

WEDNESDAY, April 1st.—Society of Public Analysts, 8. "The Bacteriological Examination of Water for the Typhoid Bacillus," by T. H. Pearmain and C. G. Moor, M.A. "Note on the Estimation of Formic Aldehyd," by Harry M. Smith. "The Composition of Human Fat," by C. A. Mitchell, B.A.

FRIDAY, 3rd.—Quekett Club, 8.

THE MANUFACTURE OF EXPLOSIVES.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1897.

THE PHOTOGRAPHIC REPRESENTATION
IN RELIEF OF A MODEL
OBTAINED BY MEANS OF THE RÖNTGEN RAYS.

By J. CARPENTIER.

IN the course of researches which I have undertaken, to combine some numerical data on the permeability of metals by the Röntgen rays, I have been led to make an experiment having as its object the photographic representation of a model in relief.

The model upon which I have operated is a bronze coin. To obtain an image of the subject which it bears, the figure, and the inscription, I placed upon this medal a slender circle of aluminium well-reheated. By the stroke of a fly-wheel I have obtained a hollow mould in aluminium of the relief of the coin. This slender mould, deposited on a frame formed of several layers of black paper, and containing a photographic plate, was submitted to the action of a Crookes phial.

On account of the fact that the hollows present a less resistance to the passage of the rays than do the projections, the corresponding parts of the proof are the blackest; the image has the appearance of a negative. Small proofs on paper, obtained by contact, have the appearance of a positive. Enlargements obtained on setting out from a positive on glass are in all respects like the proof itself.

The distinctness of these various images is very great, on account of the precaution taken to interpose between the phial and the plate an opaque screen of brass having a perforation of 1 c.m. in diameter.

The relief of the bronze coin, although concentrated in appearance, measures only 8/100th m.m. The round disc of aluminium in the parts not stamped is of $\frac{1}{2}$ m.m. in thickness.

The phial has been but little charged, and the exposure was only four hours. In order to define the intensity of the active radiation, I compared its effect on the parts of the plate not protected by the mould with the effect produced on a similar photographic plate by an ordinary candle placed at a distance of 1 metre. I found that the action of the phial, under the conditions indicated, was equal to the action of the candle for two seconds. It would be useful for comparison if experimentalists would take care to indicate the strength of the field in which they operate. It is evident that other bodies, even though non-metallic, would be suitable for the same experiment. —*Comptes Rendus*, cxxii., p. 526.

PHOTOGRAPHIC RESEARCHES ON THE
RÖNTGEN RAYS.

By AUGUSTE and LOUIS LUMIÈRE.

IF the photographic method has just attained a new success with Prof. Röntgen's experiments, it is to be expected that it will still render greater services for the study of the X rays when the photographic preparations shall be better adapted to the properties of these rays. We are now engaged with the study of their action upon sensitive substances.

We remarked at first that the Röntgen rays act in the same manner upon gelatino-bromide plates coloured and rendered sensitive to the various spectral regions. Thus plates sensitised for red, for yellow, or for green, give

exactly the same impression, all other things being equal, on condition that they have the same general sensitiveness for white light.

If we have photographic plates of different sensitiveness for white light, it seemed to us interesting to examine if the proportion of sensitiveness is the same for the X rays. We have operated upon preparations in which the times necessary to obtain the same impression with a constant source of luminous radiation are respectively as 1.8 and 30, and we have observed that, within the range of our experiments, these proportions are exactly preserved for Röntgen's rays.

Another series of experiments had the object of studying the absorption of these rays by sensitive strata, and of comparing it with that of luminous rays in analogous conditions. To this end we exposed, under a screen formed of letters cut out of a thin sheet of copper, a packet of 250 leaves of silver gelatino-bromide, superposed and sheltered by known methods from the luminous rays. We allow the X rays to act for ten minutes, when we find, on developing, that the 150th leaf still presents an impression.

In order to judge of the importance of the absorption due to the passage of the rays through the paper serving as a support for the silver gelatino-bromide, we compared the images obtained on substituting, in the foregoing experiments, paper not sensitised for the gelatino-bromide paper. After a series of trials, we found that about 300 leaves of white paper were required to produce the same absorption as 150 leaves of sensitive paper. The layer of gelatino-bromide employed absorbs, therefore, the X rays in the same manner as the paper which serves as its support. The absorption of the X rays by sensitive paper is therefore exceedingly feeble. This property may even serve as a characteristic of these rays. If, in fact, we seek to reproduce the same series of experiments with different sources of light,—sun-light, the electric light, the Auer burner, &c.,—we find that, after passage through a very small number of sensitive leaves, the light has no action upon the subjacent papers.

The first proof having been attained with sun-light, with an impression comparable to the first leaf of the former experiment, we find that the sixth leaf no longer presents a trace of an image.

This extraordinary penetration of the X rays, and their very slight absorption by sensitive preparations, seems to afford a method of searching for these rays in sources of light of greater or less intensity. Except Crookes tubes, and similar tubes, the photographic effects which we have observed with the electric arc, the Auer burner, the petroleum lamp, &c., are due only to the penetration of the luminous rays properly so called, or to heating thermic rays, which are very rapidly extinguished by the folds of paper.

We have never been able to find the presence of X rays in these sources of light.—*Comptes Rendus*, cxxii., p. 382.

DIFFUSION OF THE RÖNTGEN RAYS.

By A. IMBERT and H. BERTIN-SANS.

IN the course of experiments undertaken in order to increase the intensity of the sheaf of Röntgen rays utilised in photography, we have observed very definite phenomena of diffusion, the existence of which seems able to contribute to a determination of the nature of the new rays.

In order to observe the existence of the diffusion we have received the rays emanating from a Crookes tube upon plane plates of different bodies, and we have arranged at the side of the tube a sensitive plate, covered with a double coat of needle-paper, in a direction nearly normal to that which the mean region of the sheaf would have if it reflected regularly. A thick plate of copper was interposed between the Crookes tube and the photographic

plate, in order to screen the latter from any direct radiation.

To prove the existence of the Röntgen rays sent back by the reflecting or diffusing plate, we fixed upon the photographic plate a crystal of quartz (opaque to these rays) fixed in a setting of cork (transparent to the same rays); a member of a metallic class (and consequently opaque) was, besides, each time interposed between the paper covering the sensitive plate and the surface of the setting of cork in contact with the paper.

Many comparative experiments have, further, been made on the same plate, protecting successively the different parts of the latter by means of thick metallic plates absolutely opaque.

We have used at first, as a reflecting or diffusive body, one of the metal plates of an Æpinus condenser, and we have found that, after an exposure of ten minutes, the photographic plate was distinctly acted upon by the Röntgen rays, whether the plate insulated by its glass foot was or was not covered with varnish, or was connected with earth or with one or the other pole of a Wimshurst machine giving sparks of 10 c.m. In each of these cases the plate has been acted on with an equal intensity, the quartz has always remained opaque, the cork always transparent, and the number of the metallic series has always been reproduced through the cork. Further, in the comparative experiment made with a fourth of each plate, causing the Crookes tube to act but suppressing the metallic plate, we have never obtained any impression or proof that our plates were entirely protected against direct radiation.

Identical results were obtained on substituting a plate of paraffin for the metal plate.

On the contrary, a plate of cork of 7 m.m. in thickness, very transparent to the Röntgen rays, gave only a scarcely perceptible impression of the number of the metallic series. It was the same with plates of glass, although this substance is relatively very opaque to the Röntgen rays; the quantity of diffused rays has also been scarcely more considerable with ground glass.

In another set of experiments we caused the Röntgen rays to traverse a glass tube of 0.12 metre in length, closed with two stoppers of cork covered with paraffin, in which a vacuum could be produced. The intensity of the photograph of a fine metallic grating was scarcely greater when we made in the tube a vacuum of 6 m.m. of mercury.

On attempting to cause a slender sheaf of rays approximately parallel, obtained by the aid of two circular diaphragms of the same diameter to be reflected from a polished metal plate, the sensitive plate, after exposure for half an hour, presented no visible trace of impression.

Hence there is room to infer that if the Röntgen rays are reflected regularly under the conditions of our experiments, this takes place only to a very slight degree. On the contrary, they may be diffused in a very great quantity, and the diffusion appears to depend more on the nature of the substance than on the degree of polish of the diffusing substance. This fact would lead us to ascribe to the new rays a very small wave-length, such that it is not possible to realise the degree of polish necessary for determining their regular reflection.

The proofs obtained have further shown us, as regards cork and quartz, the different degrees of transparency of the different bodies employed for diffused rays. We reserve it to ourselves to check this last result, and we have commenced for this purpose a series of experiments by which we hope, either by diffusion or transmission, to obtain information on the homogeneity and the complexity of the sheaf of the new rays.—*Comptes Rendus*, cxxii., No. 9.

New Series of Sulphophosphides: the Thiophosphites.—M. Ferrand.—The author has obtained and examined the cuprous, ferric, silver, nickel, chromium, cadmium, mercury, and aluminium salts.—*C.R.*, cxxii., No. 10,

THE COMPOSITION OF WATER. A SHORT BIBLIOGRAPHY.

By T. C. WARRINGTON, B.A.

(Continued from p. 146).

III. Gravimetric Methods.

A. The Combination of Weighed Quantities of Hydrogen and Oxygen to form Water (Weighed in some cases).

(29). 1889. Lord RAYLEIGH.

"On the Composition of Water." (Read March, 1889).

Proc. R. S., (1888-9), xlv., p. 425.

Chem. News, (1889), lix., p. 147.

Abs. J. C. S., (1890), lviii., p. 330.

Beibl. Wied. Ann., (1890), xiv., p. 2.

The gases were weighed in globes, from which they were pumped into a eudiometer and there burnt.

(30). 1891. E. H. KEISER.

"On the Atomic Weight of Oxygen." (March, 1891).

Amer. Chem. J. (1891), xiii., p. 253.

Chem. News, (1891), lxiii., p. 197. (Reprint).

Abs. J. C. S., (1891), lx., p. 1154.

Beibl. Wied. Ann., (1891), xv., p. 679.

The author, after criticising the work of Noyes (46) and defending himself goes on to make a complete synthesis of water by leading oxygen into a vessel containing a weighed amount of hydrogen condensed in palladium.

(31). 1891. E. W. MORLEY.

"Synthesis of Weighed Quantities of Water from Weighed Quantities of Oxygen and Hydrogen Gas."

Proc. Amer. Ass., (1891), xi., p. 185.

(32). 1895. E. W. MORLEY.

"On the Atomic Weight of Oxygen. Synthesis of Weighed Quantities of Water from Weighed Quantities of Hydrogen and Oxygen."

Amer. Chem. J., (1895), xvii., p. 267.

A new method is described. Hydrogen from palladium and oxygen from a globe are burnt together in a special apparatus. Residual water and residual gas are separately measured, giving the ratio of oxygen and hydrogen forming water. A second ratio is obtained from the weight of water and weight of hydrogen, and a third from densities of hydrogen and oxygen and determination of their combining ratio by a method similar to that of Leduc. The full paper will appear in the "Smithsonian Collections."

B. Combination of a Weighed Quantity of Oxygen with Hydrogen to form a Weighed Quantity of Water.

(33). 1820. BERZELIUS and DULONG.

"Nouvelles Déterminations des Proportions de l'Eau, et de la Densité de quelques Fluides Elastiques."

Ann. Chim. et Phys., (1820), xv., p. 386.

Schweigger Journ., (1820), xxix., p. 83.

Thomson's Ann. Phil., (1821), ii., p. 48.

Tulloch, Phil. Mag., (1821), p. 203.

The method followed is that more generally known by the name of Dumas.

(34). 1842. DUMAS.

"Recherches sur la Composition de l'Eau."

Ann. Chim. et Phys., (1843), [3], viii., p. 189.

Compt. Rend., (1842), xiv., p. 537.

Journ. Prakt. Chem., (1842), xxvi., p. 449. (Trans.).

Pogg. Ann., (1842), lvii., p. 150.

(35). 1842. ERDMANN and MARCHAND.

"Ueber die Atomgewichte des Wasserstoffes und des Calciums."

Journ. Prakt. Chem., (1842), xxvi., p. 461.

The method followed is that of Berzelius.

(36). 1842. Dr. CLARK.

"On the Revision and more Exact Determination of Atomic Weights. (Extract from a Letter).

Proc. Chem. Soc., (1842), i., p. 15.

Phil. Mag., (1842), [3], xx., p. 341.

A correction is applied to Berzelius's results to reduce weighings in air to weighings *in vacuo*.

(37). 1884. T. HILDITCH.

"On the Determination of the Atomic Weight of Oxygen."

Chem. News, (1884), xlix., p. 37.

Beibl. Wied. Ann., (1884), viii., p. 342.

The author points out the errors in Dumas' work due to use of impure hydrogen and to not weighing *in vacuo*.

(38). 1890. W. DITTMAR.

"On the Gravimetric Composition of Water." (Preliminary communication. Read Feb. 3, 1890).

Proc. R. S. E., (1891), xviii., p. 320.

Chem. News, (1890), lxi., p. 75.

Beibl. Wied. Ann., (1890), xiv., p. 435.

The author criticises Dumas' calculation of results. In the reprint in CHEM. NEWS considerable additions are made to the original paper.

(39). 1891. W. DITTMAR and J. B. HENDERSON.

"On the Gravimetric Composition of Water."

Proc. Phil. Soc. Glasgow, (1890-1), p. 1.

Chem. News, (1893), lxvii., pp. 54, 68, 77, 90, 104, 115, 126, 139, 151, 164.

Abs. J. C. S., (1893), lxiv., p. 410.

Beibl. Wied. Ann., (1892), xvi., p. 1.

Dumas' work is critically repeated, and a new synthesis is made by a modification of the method.

(40). 1892. A. LEDUC.

"Sur la Composition de l'Eau et la loi des Volumes de Gay-Lussac. (Note).

Compt. Rend., (1892), cxv., p. 41.

Abs. J. C. S., (1892), lxii., p. 1271.

Beibl. Wied. Ann., (1893), xvii., p. 994.

The method of Dumas is adopted with slight modifications.

(To be continued.)

VOLUMETRIC ANALYSIS OF A MIXTURE OF CHLORIDES, HYPOCHLORIDES, AND CHLORATES.

By AD. CARNOT.

It is known that chlorine acting upon alkaline and alkaline-earth hydrates gives rise to chlorides, and at the same time to chlorates, or to hypochlorates, according as the temperature and the concentration are higher or lower. In average conditions the three kinds of salts are formed simultaneously.

A mixture of the same salts is produced if we submit solutions of sodium chloride to electrolysis, according to the processes recently tried for the manufacture of free chlorine and of caustic soda, or of chlorates or hypochlorites.

In these various cases it is of great industrial importance to determine easily the proportion of each of the salts present.

An analogous question occurs when we require to determine the true composition of a chloride of

lime, as this product always contains a little chlorate, even when the sample has been recently and carefully prepared (Lunge and Schoch), and the proportion of this salt increases progressively with time (Pattinson), especially when the bleaching lime has been manufactured with lime partly carbonated (Fresenius).

For the analysis of such a mixture of salts I believe that I may recommend the subjoined method as at once expeditious and accurate. All the determinations are performed successively upon one and the same specimen of the saline solution.

I. We first determine the hypochlorite by the well-known method with sodium arsenite slightly modified. I have satisfied myself that in the conditions of the experiment this reagent exerts absolutely no reductive action upon the chlorate, the liquid being neutral or alkaline.

2. We then acidify with sulphuric acid and add a measured quantity of ferrous sulphate, the excess being titrated with permanganate. We thus determine the chlorate from the quantity of oxygen which it yields up to the ferrous sulphate.

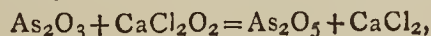
3. Lastly, we determine the total chlorine (derived either from the original chloride or from the reduction of the hypochlorite and the chlorate) by the process with silver nitrate and ammonium sulphocyanide. This process permits us to operate in an acid liquid, like that obtained by the foregoing operation.

Knowing by the two first operations the exact proportions of hypochlorite and of chlorate, we thence deduce the corresponding quantity of chlorine; the last operation then shows, by difference, the quantity of chlorine which existed in the original liquid in the state of chloride. There is no inconvenience here in making use of a determination by difference, since it applies to the salt most abundant and the least important to be exactly determined.

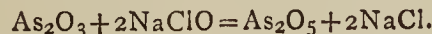
After these general indications, I must give some details concerning the manner of effecting the three successive determinations.

I. The mixture of hypochlorite, chlorate, and chloride taken from the solution of electrolysed sodium chloride, or from the liquid obtained on lixiviating the bleaching lime, is poured into a test-glass. There is then run into it from a graduated burette a standard solution of sodium arsenite, prepared as usual, until the hypochlorite is completely reduced. To find the exact moment when the reduction is completed, we place, with the end of a glass rod, a drop of the liquid upon a porcelain plate in contact with a drop of a solution of potassium iodide and of starch, prepared beforehand by stirring up in cold water 3 grms. starch, raising it to ebullition whilst stirring, adding 1 gm. sodium carbonate, and 1 gm. potassium iodide, and diluting to 500 c.c.

On the mixture of the two drops there appears a blue colour as long as there remains any hypochlorite not reduced. As soon as the mixture ceases to become coloured, we read off the volume of the arsenite liquid, and thus infer the proportion of hypochlorite of hypochlorous acid which has transformed it into arsenic acid; or, consequently, that of the chlorine corresponding.

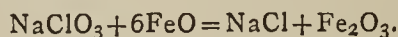


or—



II. We slightly acidify the liquid (which now contains merely chlorate and chloride) with sulphuric acid, and dissolve in it ammonium-ferrous sulphate, in a quantity at least twenty times that of the supposed chlorates. These we heat to about 100°, adding in small successive quantities 5 c.c. of sulphuric acid diluted with 15 c.c. of water. It is best to use a cock-funnel, letting the sulphuric solution fall in drop by drop. After having stoppered the vessel, to avoid contact of air, it is allowed to cool for a short time, and the excess of ferrous salt is then titrated with permanganate. As we know the quantity of ferrous salt which was introduced, we have by dif-

ference the quantity which has been peroxidised at the expense of the chlorate reduced to the state of chloride.



It is thus easy to calculate the proportion of chlorate or of chloric acid, or the corresponding quantity of chlorine.

III. As for the total chlorine, which is now entirely present in the state of chloride, it is determined as follows:—We first remove the rose tint produced by the permanganate by adding a trace of ferrous sulphate, crystallised or in solution. We then add a measured volume of silver nitrate, more than enough to precipitate all the chlorine, and determine the excess of the silver salt by means of ammonium sulphocyanide which has been standardised against silver nitrate. The ferric salt previously formed by the peroxidation of the ferrous salt serves as an indicator, by producing a permanent red colouration as soon as there is no more silver salt to precipitate. As for the arsenic acid produced in the first operation it does not interfere in the least.

In order to avoid the use of too large a quantity of silver nitrate, which would be necessary on account of the large proportion of chlorine to be precipitated, we may make use only of an aliquot part of the solution.

The chlorine found in the state of a chloride in the original liquid is easily calculated by deducting from the total chlorine just determined the two quantities already found in the state of hypochlorite and of chlorate.

The three operations succeed each other without interruption, and without separate preparation, and are completed in a short time. It is useful to check the results by making a second series of determinations to avoid accidental errors.

Numerous experiments have permitted me to find that the method yields results of great accuracy. These experiments have been made with known and very varied quantities of the three salts taken separately, or two by two, or all three taken together. The chlorides and chlorates were weighed in a state of purity; the chloride of lime, which has always a complex composition, was treated with water, and the lixivium was assayed first for hypochlorites, chlorate, and chloride, and it was then assayed anew after the addition of known quantities of alkaline chlorate and chloride.

The discrepancies found between the experimental results and the calculated numbers rarely reached 1 m.grm. when operating upon from 250 to 500 m.grms.—*Comptes Rendus*, cxxii., p. 449.

GAS ANALYTICAL APPARATUS FOR THE EXAMINATION OF AIR CONTAINING FIRE-DAMP.

By SIGMUND REICHENBERG,
Royal Hungarian Inspector of Steam-boilers.

THE apparatus is constructed on the principle of Coquilhon's apparatus. Fig. 1 is the elevation. Instead of the bottle, which in ordinary apparatus for gas-analysis contains the closing-liquid, there is employed here a caoutchouc globe, *c*, which is compressed or allowed to expand by turning the screw, *s*, to the right or the left, and the mercury which it contains rises into the measuring pipette or flows back. The movement of the screw is taken up by the rod *d* by means of the tube *t*. The measuring pipette, *M*, and the caoutchouc ball, *c*, are immersed in the glass cylinder, *G*, which is filled with water. The measuring pipette, *M*, communicates as usual with the atmosphere (but is capable of being shut off), and with the absorption tube, *A*. At *S*₁ and *S*₂ there are screw-clamps for the caoutchouc tubes serving for communication.

Fig. 2 shows the combustion tube (*B*, Fig. 1) in actual size; *P* is the spiral of platinum wire, which can be made

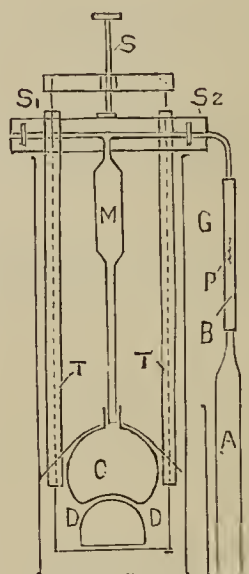


Fig 1

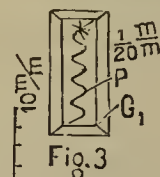


Fig. 3

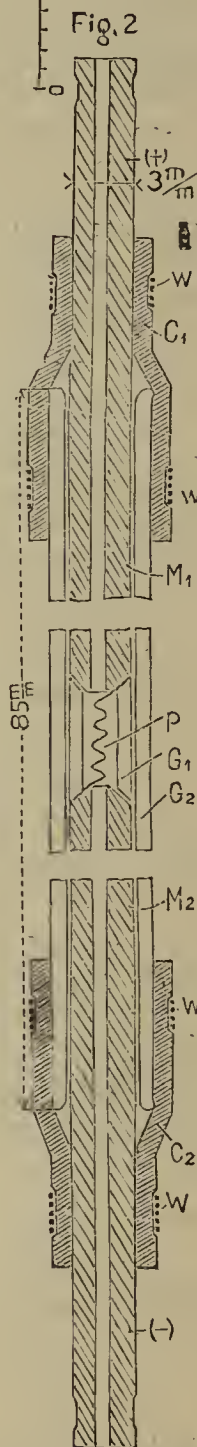


Fig. 2

red-hot by a galvanic current. The current is conducted by the metal tubes *M*₁ and *M*₂. Through these tubes there flows simultaneously the air containing methane out of the measuring pipette *M* (Fig. 1) into the absorption tube (*A*, Fig. 1) and back again; whereby the methane is completely burnt by close contact (twice repeated) with the ignited platinum spiral. The conical (or rather, globular) ends of the metal tubes, *M*₁ and *M*₂, fit suitably in the ground glass apertures of the small glass tube, *G*, in which the contact of the metal tube takes place with the platinum spiral. To ensure stability, the ends of the platinum spiral are bent over around the edges of the small glass tube, as shown separately in Fig. 3. The glass tube, *G*₂, which infolds the metal pipe, is closed by

the caoutchouc tubes C_1 and C_2 . For a more thorough closure, the caoutchouc tubes are connected with thin wire, w . Before applying the fourth wire binding the caoutchouc tube concerned is drawn up and the wire binding is applied while it is in this state of tension. In this manner the elasticity of the caoutchouc tube presses the ends of the metal tubes, M_1 M_2 , into the mouths of the small glass tube, G , where there arises better contact for the conduct of the galvanic current with the platinum spiral. The conductive wires of the galvanic current are connected with the metal tube at $+a-$. The absorption tube (Fig. 1, A) contains a weak alkaline solution, to absorb the carbonic acid generated. The absorption tube is, as usual, filled with glass piping.

Before the measurement takes place, the air under examination is passed from the measuring pipette into the absorbent tube, where the air is saturated with moisture. The decrease of volume after the combustion of the methane divided by 3 gives the proportion of methane.

To avoid errors in measurement the internal parts of the apparatus, especially the combustion-tube, should be kept clean.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 149).

CHAPTER IX.

CHEMICAL RESEARCHES ON SULPHATE, SULPHIDE, CHLORIDE, AND CARBONATE OF BARIUM.

I HAVE tried, at different times, to obtain pure chloride of barium for the purpose of determining its molecular combination with silver. The discordance in the results arrived at, with chloride made in different ways, prevented me from publishing my research. I worked in 1858 upon chloride of barium obtained in large quantities by the late M. Kuhlmann. I have prepared it myself from witherite. I found, then, that I could not entirely eliminate strontium and calcium from chloride of barium by the method of successive crystallisations. I succeeded no better by taking up the chloride of barium in boiling alcohol. Acting on Bunsen's advice, I took up the research again in 1863 and 1866, and again failed to arrive at concordant results, that is within the limits of accuracy possible when using alkaline chlorides. Having at last discovered the cause of the divergence in my results, I made another attempt to obtain pure chloride, but intended this time for quite a different purpose—that of ascertaining whether, by the action of heat, the barium spectrum could be changed into that of strontium, calcium, sodium, or lithium.

When I applied spectrum analysis to the research on the purity of barium compounds, I found that the chloride of barium obtained by successive crystallisations, however many times repeated, persistently showed a sodium spectrum, and that the carbonate obtained by precipitating this chloride by means of sesqui-carbonate of ammonium, persistently showed traces of the sodium and calcium spectra. The fact is that, by carrying on the operations in glass vessels, I was constantly attacking the constituents of the glass, and thus introduced silica, soda, and lime into the compounds formed. Having found the source of error, I was enabled to see in what direction to push my investigations.

I commenced with chloride of barium, prepared in large quantities by the late M. Kuhlmann, or made by myself by dissolving witherite in dilute hydrochloric acid. I first eliminated the iron, manganese, and lead in the chloride, by means of a slight excess of sulphhydrate of barium. Complete separation was effected when working in a solution kept boiling for from fifteen to twenty minutes. After filtration, the liquid, slightly

acidulated with hydrochloric acid, was concentrated to saturation, and then quickly cooled. The chloride was *crystallised ten times*, reserving the mother-liquor and the washings each time.

I treated this chloride five times with a 98 per cent solution of boiling alcohol. I found in the residue left after distilling the alcohol, besides barium, calcium, strontium, and sodium. The chloride, when put into a Bunsen flame on a platinum wire loop, gave it the sodium colour, and the sodium line continued visible so long as the residue from the decomposition remained in the flame.

To eliminate the silica contained in chloride thus treated, I had recourse to the method I employed for freeing the chlorides of calcium and strontium from silica,—that is to say, to the action of chloride of ammonium at a high temperature. I put it all, when dried by means of alcohol, into a platinum retort, and moistened it with a solution of pure chloride of ammonium. After desiccation, the mixture was heated till the greater part of the sal ammoniac was driven off. The chloride was taken up in just enough cold water to dissolve it, and the slightly clouded solution was filtered to separate the suspended silica.

I repeated the treatment with chloride of ammonium twice more, and on the third occasion the chloride, when dissolved in water, formed a perfectly clear liquid, leaving no trace of silica on the filter.

When this stage was reached, the solution was divided into two parts, A and B.

The part A, diluted with five times its volume of water, was poured into its own volume of water containing enough pure sulphuric acid to precipitate all the barium. The part B, also diluted with five times its volume of water, was poured into an equal volume of a dilute solution of sulphate and sesqui-carbonate of ammonium, in a covered platinum vessel, and containing enough sulphate to precipitate all the barium.

The barium, calcium, and strontium ought to be entirely in the form of sulphates in the A precipitate, whilst in the B precipitate—the barium only could be in the form of sulphate—the calcium and strontium ought to be found in the form of carbonates.

The sulphates, having been formed in a very dilute liquids, were extremely finely divided, and remained in suspension a very long time. Their washing, which had to be done by decantation, occupied *several months*. The washing of the sulphate formed in the ammoniated medium was the most difficult, and took the longest time. It showed this peculiarity, that the washings, though quite clear, were clouded by the addition of a few drops of nitric acid, as though sulphate of barium was present, owing to the action of the sulphate of ammonium. But, whatever the cause of the fact might be, I frequently noticed it during the first washings.*

In the small residue left after evaporating the mother-liquors, and in the decantation water from both the precipitates A and B, I detected barium, calcium, strontium, and sodium.

After washing, I put the sulphate from A into a large platinum vessel; I moistened it with a saturated solution of sesqui-carbonate of ammonium, and left the solution to itself for twenty-four hours, sheltered from air-dust, to transform the calcium and strontium possibly still remaining in it into carbonates.

I diluted the sulphate from B with its own apparent volume of water containing 5 per cent of distilled hydrochloric acid, and I left this also to itself for twenty-four hours.

After this interval both the A and B sulphates were suspended in water, and left to settle. A very long time was required before this result was reached, and all the difficulties met with in the washings by decantation occurred again. I could find no other method of saving

* These researches were carried on in 1879; since that time sulphate of barium has been found to be soluble when precipitated in sulphate of ammonium.

time than by getting rid, at each washing, of a small part of the sulphate which had already been the cause of so much work.

After washing the precipitate from A, I treated it with water acidulated with hydrochloric acid, as I had done with the precipitate from B, and then washed it afresh with pure water.

The water acidulated with hydrochloric acid, which had held the sulphates of barium from A and B, contained barium and traces of calcium and strontium, and a great deal of sodium.

I kept the sulphates from A and B in suspension in boiling water in a platinum vessel, and however long they were kept in, and however often the water was renewed, the introduction of a portion from A and B into a Bunsen flame always had the initial effect of colouring the flame *yellow*. I had therefore to acknowledge that I was unable to free either of these sulphates of barium, most carefully and perseveringly treated, from sodium, so far that at the instant of contact it would not impart a yellow colour to a Bunsen flame or oxyhydrogen blowpipe. After trying the experiment sufficiently often in pure air, the sulphates were dried in the platinum vessels which held them, at first on a water-bath, and then at a high temperature. By the action of heat they were considerably contracted, remaining perfectly white. This effect can only be shown in platinum when never putting the metal into contact with water containing more than 5 per cent of its volume of hydrochloric acid.

Immediately after their desiccation, or after they had been kept under a bell-jar of pure air, kept dry by sulphuric acid, the sulphates imparted to flames a yellow colour, neither more intense nor more persistent than when moist. It follows, from these observations, that sodium combines with sulphate of barium in a still more marked degree than with the carbonates of calcium and strontium, and *at least* as strongly as with carbonate of lithium. But under the combined influence of heat and a current of gas, sodium can be eliminated with as much ease as the carbonates of calcium and strontium, and much more rapidly than carbonate of lithium.

Both sulphates, when freed from sodium in an oxyhydrogen blowpipe, imparted to this flame the green colour characteristic of barium compounds. When heated so far as to melt first, and then partially solidify by dissociation, they showed the well-known barium spectrum, as I describe in the next chapter. Neither at a low temperature, nor at the fusing-point of iridium, did they show any trace of the lines characteristic of the calcium, strontium, lithium, potassium, or sodium spectra.

In 1866 I reduced to sulphide some sulphate of barium obtained by the two methods I have just described. I effected this reduction by mixing the sulphates with pure petroleum black, and heating the mixture in a covered carbon crucible contained in a porcelain crucible, filled with charcoal that had been purified by hydrofluoric and hydrochloric acids.

Either on account of silica and soda from the fire having penetrated inside the crucible during the heating, or from some other unknown cause, the fact is that both sulphates showed a barium spectrum in an oxyhydrogen blowpipe with hydrogen in excess, in which *the sodium spectrum appeared continuously*.

I then reduced sulphate of barium by means of pure hydrogen. For this purpose I filled with sulphate a platinum boat, recently heated in a hydrogen and air blowpipe, contained in a large boat of pure carbon. I put this apparatus into a large porcelain tube, heated to a dull red heat, through which pure dry hydrogen had already been passing for some time. After the reduction I maintained the current of hydrogen until the tube was quite cold.

The sulphides were greyish white, excepting at the points of contact with the edge of the platinum boat. In an oxyhydrogen blowpipe, with hydrogen in excess, they

showed the same barium spectrum as the sulphates from which they were made, and in which the sodium spectrum was visible for some time, though it finally disappeared entirely.

In spite of the sulphide of barium attacking the platinum, I reduced, in a sheet of pure platinum shaped into a boat, a considerable quantity of sulphate, from which I had eliminated as far as possible all the sodium, in an oxyhydrogen blowpipe. Without withdrawing the boat containing the sulphide from the porcelain tube, I passed through it, at first in the *cold*, a current of pure and dry hydrochloric acid. When the greater part of the sulphide was thus transformed into chloride, I raised the tube to red heat, in the current, so as to make sure of having decomposed the whole of the sulphide of barium.

The chloride thus made, when introduced at once into an oxyhydrogen blowpipe, showed a very strong and brilliant barium spectrum, the same as that of the sulphate and sulphide, in which the sodium spectrum appeared *very temporarily*; this latter disappeared long before all the chloride was reduced to the state of oxychloride.

I dissolved in water a certain amount of the chloride thus made in platinum, in order to transform it into carbonate. This salt, obtained by double decomposition with the dilute solutions, being very difficult to wash, I hoped, as really was the case, to succeed more easily by passing a current of carbonic acid into a solution of ammonia containing chloride of barium. For this purpose I dissolved some ammonia in the solution of chloride of barium contained in a platinum dish, carelessly passing the gas through an *ordinary glass* tube, and, as soon as the liquid smelled strongly of ammonia, I passed into it a current of carbonic acid until all the barium was precipitated. The carbonate made thus was comparatively easy to wash; but after thoroughly washing it, and introducing it into a Bunsen flame or an oxyhydrogen blowpipe, it showed the sodium line *persistently*. The contact of ordinary glass with dissolved ammonia was sufficient to introduce into the salt a very small quantity of silicate of sodium, sufficient however, to render the complete elimination of this element almost impossible. I should add that, when dissolving silicate of sodium from the glass, it also combined with traces of calcium. I found that, at the fusing-point of iridium, spectrum analysis of an oxyhydrogen blowpipe showed transient, but distinct, traces of the blue calcium line, in addition to the barium and sodium spectra.

I might have omitted to mention the mistake I made; but I thought that the lesson it teaches might be useful to any person trying in the future to check these researches.

I was obliged, therefore, to re-commence the preparation of carbonate of barium in platinum, without using glass: this is very easy, because in default of platinum tubes to replace those of glass, one can use rubber or even gutta-percha tubes weighted with platinum, which have remained for some time in dilute hydrochloric acid, as I have done both before and since. Taking every precaution to protect it from air dust, I then precipitated an ammoniated solution of chloride made from sulphide, by means of carbonic acid. I washed the resultant carbonate of barium by decantation, first with cold water, then with boiling water, until the chlorine was entirely eliminated.

Immediately after the washing, the still moist carbonate, when introduced into a Bunsen flame, gave it very temporarily the sodic characteristics; but it was hardly brought to a bright red heat in an oxyhydrogen blowpipe before the sodium line disappeared, and was not afterwards visible, even at the fusing-point of iridium.

I treated this carbonate with water containing carbonic acid, but I was not able thus to weaken the slight sodic character it gave momentarily to an oxyhydrogen blowpipe flame.

After being dried in platinum, and kept for a long time

under a bell-jar protected from air dust, this carbonate showed a stronger sodium spectrum, but the sodium line faded very rapidly and left the barium spectrum only, when the air itself did not show any traces of the former.

(To be continued).

ON THE INVERSION OF SUGAR BY SALTS.*

By J. H. LONG.

It is a well-known fact that the specific rotation of solutions of cane-sugar is decreased by the presence of many neutral salts, even by sodium chloride and other salts of the alkali and earth groups. The amount of this decrease has been measured by several chemists, and recently very carefully by K. Farnsteiner (*Ber. d. Chem. Ges.*, xxiii., 3570), who has noted the connection between the molecular weights of the salts dissolved with the sugar and the amount of the depression they produced. In a solution containing for each part of sugar 3 parts of water and 1.0036 parts of sodium chloride the specific rotation dropped from 66.6° to 62.47° . Similar effects were observed in other cases.

The extent of this depression is dependent to some degree on the temperature, but a temporary increase in temperature does not permanently alter the rotation. In illustration, a solution of pure saccharose, containing in 100 c.c. 25 grms. of the sugar and 10 grms. of potassium nitrate, gave a specific rotation of $\alpha_D = 66.22^\circ$ at 20° . After heating one hour, but so as to avoid evaporation or pressure, the rotation was again determined, and found to be practically the same. The solution was heated in a small flask closed with a perforated rubber stopper, having a capillary glass tube in the perforation. It was possible by this means to heat the liquid to 100° in boiling water without risk of appreciable loss by evaporation.

On the other hand, a solution of sugar and zinc sulphate which gave a specific rotation of 64.98° when fresh, showed, after having been heated forty-five minutes in boiling water, as before, a specific rotation of 36.84° . In this case a decided inversion had taken place, as easily shown by other tests. The behaviour of zinc sulphate is similar to that of a large number of other substances. Loewenthal and Lenssen (*Jsb. Chem.*, 1863, 120) and Ostwald ("Allg. Chemie," ii., 811) state that zinc sulphate and other neutral salts are without inverting action; but Béchamp, a little later (*Jsb. Chem.*, 1864, 573), and Gmelin ("Handbuch der Org. Chem." iv., 1, 691), gave a list of these salts which are able to produce a marked inversion. The phenomenon is an interesting one, and one which can now be easily explained, but until quite recently the literature has been almost silent on the subject. I wish to present in what follows a few observations bearing on the question.

Over a year ago, in giving instruction to a class of students on the use of the polarimeter, I suggested, as an illustration of a substance for examination, not free from colour, the syrup of ferrous iodide of the pharmacopœia. Instead of exhibiting a more or less marked right-hand rotation, as was expected, it was found to be strongly levo-rotatory. The syrup, however, was known to be old, and had been exposed to the light. As a certain practical interest attaches to the question, it was decided to investigate fresh solutions.

The syrup of the pharmacopœia is made to contain in 100 c.c. about 63 grms. of sugar and 13.4 grms. of ferrous iodide. On January 19th, 1895, a litre of this solution was made according to the usual process, special care, however, being taken in the selection of the sugar and iodine employed. The liquid polarised immediately, in a 200 m.m. tube, gave $\alpha_D = 81.15^\circ$ at 20° . Four days later

the rotation was found practically unchanged, the syrup having been kept meanwhile in the dark. A bottle holding about 100 c.c., and furnished with a glass stopper, was then filled with the syrup and allowed to stand until May 6th, and exposed to diffused light. This portion now showed, on polarisation, $\alpha_D = 53.12^\circ$ in the 200 m.m. tube, while the original, kept in the dark, polarised 63.17° . On this date, May 6th, a second portion of the original was filled into a bottle and allowed to stand in the light. It was polarised at different intervals, with results as follows, at 20° , in the 100 m.m. tube:—

July 15th	α_D	+ 6.66°
Aug. 24th	"	- 4.36°
Oct. 22nd	"	- 13.10°
Nov. 15th	"	- 13.42°

Another portion of the original, which had stood since Jan. 19th in a small full bottle in the light, gave now, in the 100 m.m. tube, $\alpha_D = -15.66^\circ$. From this it appears that in the interval the saccharose had undergone complete inversion. The original rotation observed, 81.15 , was that of a solution in which some inversion had already taken place.

Another solution was prepared on May 9th, containing, in 250 c.c., 140 grms. of sugar and an amount of ferrous iodide corresponding to 28 grms. of iodine. The syrup and iodide solution were hot when mixed. This polarised at 20° gave a rotation of 33.25° in the 100 m.m. tube, which corresponds to a specific rotation of 59.38° . At intervals the following rotations were found from two portions of this solution, which had been poured into glass-stoppered bottles and kept in the light. One bottle was full and the other not quite full.

		Full bottle.	Partly filled.
July 13th	α_D	18.66°	+ 9.30°
Aug. 24th	"	8.58°	+ 3.56°
Oct. 22nd	"	3.76°	- 10.16°
Nov. 15th	"	2.70°	- 10.75°

It is apparent from the above that the presence of air in the bottle with the solution has a marked influence on the rapidity of inversion.

Influence of Temperature.

The solution just described stood at the laboratory temperature during the time of the observations. A marked decrease in the time required for full inversion would naturally be expected by working at a higher temperature. This was shown by heating some of the last solution in boiling water during ninety minutes. The solution was contained in a flask with a capillary stopper. Before heating it had a rotation of 33.25° in the 100 m.m. tube; after the application of heat the reading was -12.75° in the same tube. The following day the solution was re-heated through three hours and polarised again, giving now -13.00° at 20° . Heating through ninety minutes was therefore sufficient to complete the reaction, and it is evident that an inversion which, at the mean laboratory temperature of 20° to 25° , requires months for its completion, may be accomplished in less than two hours at the temperature of boiling water.

It was found later that a moderate increase of temperature does not greatly hasten the inversion; this becomes rapid only above 60° .

Influence of Light.

It should be remarked that the inversion by heat, as well as by long standing in the light, is accompanied by a decided loss of colour. A solution of ferrous iodide exposed to the air, or protected from the air and kept in the dark, soon becomes brown from partial decomposition and separation of iodine, which is easily shown by the starch reaction. In stoppered bottles in the light, however, this decomposition is almost wholly prevented, and in an already coloured solution in which free iodine is

* From the *Journal of the American Chemical Society*, vol. xviii., No. 2, February, 1896

shown by tests the colour is lost by exposure to the light.

Well-made undecomposed solutions of ferrous iodide are described as light green, but they may become almost as colourless as water, leaving the iron in a perfectly reduced condition. It has been found, by numerous trials, that the rate of inversion is more rapid in bottles exposed to the light than in similarly filled bottles kept in the dark. The rapidity of inversion is further increased if the solution is exposed to the action of light and heat together. More will be said of this later.

The phenomena described above are not confined to ferrous iodide, but are exhibited by many other salts. In fact, from theoretical considerations, they should be expected in some degree from the salts of all the so-called heavy metals, as will presently be pointed out. First, however, some actual experimental results will be given.

Ferrous Chloride.

A solution containing, in 100 c.c., 50 grms. of cane-sugar and $4\frac{1}{10}$ grms. of pure ferrous chloride was prepared. The ferrous salt was made by the action of an excess of iron on hydrochloric acid, and the syrup made with this and the sugar was bright green. It showed a rotation of 32.75° in the 100 m.m. tube, or a specific rotation of 65.50° . After heating one hour to 100° the rotation was found to be -6.42° in the same tube.

Ferrous Bromide.

The solution contained, in 100 c.c., 50 grms. of saccharose and 10 grms. of the bromide. The latter was made by the action of bromine and water on iron, and the solution so obtained was filtered into the dissolved sugar. The rotation of the fresh mixture was found to be 32.25° . A portion was heated one hour to 100° and was then polarised, after cooling to 20° , giving now a rotation of -10.26° .

Ferrous Sulphate.

The solution of 100 c.c. was made with 50 grms. of sugar and 10 grms. of pure crystallised sulphate. It was slightly cloudy, and could not be polarised with the greatest accuracy, but the reading was nearly 33° . A portion was heated one hour away from the air. It became clear, and could be easily examined in the polarimeter, showing now, at 20° in the 100 m.m. tube, 18.20° . This decrease is much less than in the other cases, but not unexpected.

Ferrous Ammonium Sulphate.

The solution made contained, in 100 c.c., 50 grms. of sugar and 10 grms. of the crystallised salt. When fresh it gave a rotation of 33.08° . After heating five hours to 71° the rotation was found to be 27.20° . This solution was allowed to stand in a stoppered bottle in the light, and was polarised at different intervals with the following results:—

July 24th	a_D	27.20°
Aug. 24th	„	20.22°
Oct. 22nd	„	10.23°
Nov. 15th	„	7.53°

We have here, as before, a slow rate of inversion.

Manganous Chloride.

A solution was made on July 24th containing, in 100 c.c., 50 grms. of sugar and 10 grms. of the carefully purified salt, with $4H_2O$. It gave immediately a rotation of 32.88° , and, after heating five hours to 71° , a rotation of 28.16° . From this date, July 24th, the heated portion was allowed to stand in the light at the laboratory temperature in a full bottle, and showed at intervals the following rotations, all in the 100 m.m. tube, at 20° :—

Aug. 24th	a_D	22.20°
Oct. 22nd	„	4.71°
Nov. 15th	„	1.66°

After standing a short time in the light this solution

became as colourless as water when observed in a clear glass bottle of 4 c.m. diameter.

Manganous Sulphate.

The experimental solution was made to contain, in 100 c.c., 50 grms. of sugar and 10 grms. of crystallised manganous sulphate ($MnSO_4 + 4H_2O$). The rotation was found to be 33.16° . On heating the solution one hour to 100° it became slightly decomposed and darker in colour, instead of lighter as with the chloride. The decomposition product was small in amount, but exceedingly fine and dark. It remained long in suspension, making an exact reading of the rotation impossible. It was about $+7^\circ$, however, in the 100 m.m. tube. The suspended substance was probably an oxide of manganese.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 27th, 1896.

Prof. CAREY FOSTER, Vice-President, in the Chair.

Prof. J. A. FLEMING read a paper on "The Edison Effect."

The Edison effect alluded to in the title of the paper is that, if a metal plate is placed inside the loop of an incandescent lamp, then a galvanometer, of which one terminal is connected to this metal plate and the other to the positive lead of the lamp, will indicate a current passing from the lead to the plate. If, however, the galvanometer is connected to the plate and the negative lead, no current passes.

Prof. Fleming, by connecting the poles of a condenser, —1st to the two leads, 2nd to the plate and positive lead, and 3rd to the plate and negative lead, in each case discharging the condenser through a galvanometer,—has shown that, after the lapse of a certain time, depending on the position of the plate, if the lamp is working at about four Watts per candle, the potential of the plate falls to that of the negative lead. If the plate, instead of being inside the loop of the filament, is outside, then the time taken by the plate to acquire the potential of the negative lead is considerably longer.

The space between the plate and the negative lead exhibits a kind of unilateral conductivity, for a battery having a low voltage is able to send a current from the plate to the negative lead, but not in the opposite direction. If, instead of using a cold metal plate, a second filament, maintained in a state of incandescence by an insulated battery, is used, then a current can be obtained between this filament and both the positive and negative leads.

If the voltage on the lamp is raised considerably above that required to give one candle-power for four Watts, then a current can be passed from the plate to the negative lead, while a galvanometer connected to the positive lead and the plate will indicate the passage of a current from the positive lead to the plate. When the lamp is in this condition, the space between the plate and the negative lead is very sensitive to the effects of a transverse magnetic field, such a magnetic field causing a large increase in the resistance.

The curve showing the connection between the current passing from the positive lead to the plate and the volts between the terminals of the lamp, is found to be discontinuous. As the volts are raised the current suddenly increases about tenfold, and it is while the lamp is in the condition corresponding to this upper portion of the curve that it is sensitive to the influence of the transverse magnetic field.

By using a movable plate it has been found that the minimum current is obtained when the plate is nearer the positive than the negative lead.

When an alternating current is used to supply the lamp, a continuous current can be obtained passing from the plate to either of the leads.

If a small platinum cylinder is placed surrounding each of the leads, then a current can be obtained between each of the cylinders and the positive lead, but no current between the two cylinders. The largest effect occurs when a cylinder near the end of the negative lead is connected to the positive lead.

The author considers that his experiments show that the resistance of a vacuum tube to the passage of a discharge would be greatly reduced if the kathode were made incandescent.

Prof. S. P. THOMPSON said he would like to have some information as to the state of exhaustion of the lamps; whether this was such as is found in ordinary commercial lamps, or whether it more nearly approached that used by Crookes. A great change in the conductivity, &c., took place at an exhaustion slightly greater than that ordinarily found in incandescent lamps. It would be of interest to vary the size of the kathode, and to investigate whether the magnitude of the effects observed depended on the fall of potential per unit length along the filament. Another point was whether the position of the plate for which the effect was a minimum was the same for all lamps, or whether it changed with the volts and the length of the filament employed. Again, did the minimum occur at a certain fraction of the distance between the positive and negative leads, or, as was the case in some of the phenomena observed by Crookes, at a definite distance from either of the leads? These points might be investigated by means of a lamp with a straight filament, where the fall of potential per unit length along the filament could be made the same as with the loop-shaped filament, but the fall of potential per unit length in the vacuum would be different. The author's proposed experiment of heating the kathode by concentrating on it the rays of a lamp did not seem to him (Prof. Thompson) to differ materially from Crookes's experiment in which an incandescent wire, heated by a current, was used as the kathode.

Mr. SKINNER said that the heating of the kathode by means of a "burning-glass" could easily be carried out.

Mr. BLAKESLEY pointed out that it would be quite possible to produce an increase of the current by means of a magnet.

Mr. SERLE said that Prof. J. J. Thomson had shown that a magnet affected the conductivity of a gas.

Prof. FLEMING, in his reply, said that no doubt the effects were largely dependent on the vacuum in the lamps. The lamps employed were exhausted to the ordinary commercial vacuum. Since it was found that the "treating" was more worn off the negative leg of the filament, and that a screen placed between the legs of the filament was more blackened on the side turned towards the negative leg, it would appear that the particles of carbon were shot off from the negative leg, and hence perhaps the charge was carried by these carbon molecules.

A paper of a purely mathematical character, entitled "Notes on the Electro-magnetic Effect of Moving Charges," by Mr. W. E. MORTON, was read by Mr. SERLE, who also made some remarks on his own investigations dealing with this subject.

The Society then adjourned till April 24th.

On the Röntgen Rays.—Ch. Girard and F. Bordas.—From the authors' experiments it seems to follow that the Röntgen rays emanate both from the kathode and the anode, and that the fluorescence produced on the wall of the Crookes tube acts but slightly upon sensitive plates.—*Comptes Rendus*, cxxii., No. 10.

NOTICES OF BOOKS.

Laboratory Tables for Qualitative Analysis. Drawn up by the Demonstrators in Chemistry of the Owens College. Manchester: J. E. Cornish. 1896.

THESE Tables belong to a class of publications in which the English press, during the last few years, has been sufficiently fertile. It goes without saying that the student will find here nothing erroneous. But it is, perhaps, no less true that he will encounter nothing which he might not find in works readily accessible.

The Tables are five in number, adapted for supervision on the wall of the laboratory, and treating respectively of the examination of solids, of preliminary examination for acids, and for organic substances; of the silver group, the copper group, with the arsenic group, the iron group under normal conditions, and in presence of organic, silicic, boric, hydrofluoric, and phosphoric acids; the barium group, and the magnesium group.

The thought again suggests itself to us—When will this wealth of elementary blossom ripen into a crop of discoveries?

Single-Salt Analysis. By B. P. LASCELLES, M.A., Assistant-Master at Harrow School. London: Swan Sonnenschein and Co., Ltd.

MUCH of what we have said concerning the Laboratory Tables drawn up by the Demonstrators in Chemistry at Owens College must apply also to this publication.

The student must always bear in mind that "single-salts" are not very commonly to be met with in nature or art, and that small quantities of impurities may modify—not to say mask—the reactions due to pure substances.

Repertory of Special Reagents, generally known under the Names of their Authors. ("Repertoire des Réactifs Speciaux, généralement désignés sur leurs Noms d'Auteurs.") By FERDINAND JEAN (17, Faubourg St. Denis) and G. MERCIER (158, Rue Saint Jacques). Paris: Published and sold by the Authors. 1896.

THE number of special tests which have found their way into general practice is now very great, and they are generally mentioned simply under the names of their authors. Hence MM. Jean and Mercier have rendered an important service, not merely to students, but to analytical practitioners. In the work before us we find each reagent placed under the name of its discoverer, arranged in alphabetical order. The methods of preparing and applying the tests is given, and in many cases the extent of their sensitiveness. The special tests for strychnine, brucine, &c., have been overlooked, and in some cases the names of the authors are given incorrectly. Thus for Remsen we read here Rensen; for Runge we find Range; for Letheby, Lethebey; for Warrington, Warrigton; for Griess, Greiss; for Unverdorben, Anverdorben, &c.

We have the less scruple in calling the attention of MM. Jean and Mercier, because a second edition of so useful a book may be expected as a matter of certainty.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 10, March 9, 1896.

Certain Novel Properties of the Invisible Radiations Emitted by Phosphorescent Bodies.—Henri Becquerel.—This paper will be inserted *in extenso*.

Use of Artificial Hexagonal Blende as a Substitute for the Crookes Phials.—M. Troost.—Already inserted.

Some Conditions which Govern Gaseous Combinations. Union of Oxygen and Hydrogen at Low Temperatures.—Armand Gautier and H. Helier.—A mixture of hydrogen and oxygen, after seventy-eight hours of contact, still contains about one-third of the explosive mixture uncombined. In glass tubes silvered within there ensues a total combination. Here, however, there is a secondary reaction at 450° to 480°, the silver combining with the glass and forming a triple silicate.

Yttrium and Thorium Carbides.—H. Moissan and M. Etard.—Yttria forms a carbide of the formula C_2Y . It occurs in transparent crystals decomposable by cold water, with formation of a gaseous mixture rich in acetylene, and containing methane, ethylene, and a small quantity of hydrogen. Thorium also forms a crystalline and transparent carbide, C_2Th , which is also decomposed by water, producing gaseous carbides, poorer in acetylene, but richer in free hydrogen.

Determination of the Mass of a Cubic Decimetre of Distilled Water, deprived of Air, at its Maximum Density.—J. Macé de Lépinay.—The mass of a cubic decimetre of water is 0.999954 kilo., with a possible error of 6 units of the last characteristic figure.

The rôle of the different Forms of Energy in Photography through Opaque Bodies.—R. Colson.—Already inserted.

Electric Effects of the Röntgen Rays.—Auguste Righi.

Some Facts relating to the Röntgen's Rays.—A. Batelli and A. Garbassa.—In a memoir published in the last number (January) of the *Nuovo Cimento*, we have pointed out that Röntgen rays may be obtained very brightly by rendering selected minerals fluorescent by means of the cathodic radiation. The use of Tesla's arrangement reduces the duration of the exposure. We have obtained good photographs with an exposure of two seconds only. We have indicated several substances which, on exposure to the Röntgen rays, give a fluorescence even more intense than that produced by barium platinocyanide. We have found that the time of exposure may be reduced by means of fluorescent substances placed behind the photographic plate. We have placed beyond doubt the existence of reflection and the absence of refraction.

Certain Specimens of Glass submitted to the Action of the X Rays.—V. Chabaud.—Already inserted.

Technics of Photography by the X Rays.—A. Imbert and H. Bertin-Sans.—This paper will be inserted in full.

On the Centres of Emission of the X Rays.—Prince B. Galitzin and M. de Karnojitzky.—A wood board is divided into squares, the sides of which are of 1 c.m. each; at each angle of the squares we introduce small nails of the same height. This board is placed upon a photographic plate contained in a wrapping impenetrable to ordinary light. Above the nails we arrange at a little distance Crookes tubes of various forms, tracing upon the wood the outlines of the tubes by means of a lead wire. An examination of the proofs thus obtained enables us to draw the following conclusions:—The surface of emission is very small. The centre of emission does not correspond to the surface of the tube, but is found in the interior at the distance of some millimetres from the side. It is quite possible that, beside the centre of emission corresponding to the cathode, there is another derived from the anode.

Direction of the X Rays.—Abel Buguet.—This paper will be inserted in full.

Thermochemical Study of the Amides and the Ammoniacal Salts of certain Chlorinated Acids.—Paul Rivals.—Not suitable for useful abridgment.

Photography in Colours. Substitution of Organic Colours for the Reduced Silver of Photographic Proofs.—Georges Adolphe Richard.—This memoir will be inserted as soon as possible.

Action of Nitrogen Peroxide and of Air upon Bismuth Chloride.—V. Thomas.—The compound obtained has a composition answering to the formula $BiOCl$.

Modifications introduced into the Methanometer ("Grisoumeter"), and on the Limit of Approximation which it can Reach.—J. Coquillion.—For small proportions of combustible gases this instrument is very accurate. The observer can obtain an approximation of 1/1000th.

Detection of Argon in the Natatory Bladder of Fishes and Physaliæ.—Th. Schloësing, jun., and Jules Richard.—The presence of argon is shown in these gases, but it does not seem to play any perceptible part in the economy of these animals.

Determination of the Acidity of Pyroligneous Products.—M. Scheurer-Kestner.—The specimens of crude pyroligneous acid which the author has studied contain up to 17 per cent of their total acetic acid in the form of methyl acetate, and a quantity of phenolic compound corresponding to larger quantities of acetic acid.

Certain Derivatives of Triphenylsilicoprotane.—C. Combes.—Not suitable for useful abridgment.

Russian Oil of Aniseed.—G. Bouchardat and M. Tardy.—Russian oil of aniseed contains an enormous proportion of anethol, very small quantities of anisic anhydride, anisic acetone, anisic camphor, and various carbides of the formula $C_{30}H_{24}$. All these substances do not amount to more than the twentieth part of the anethol.

MISCELLANEOUS.

On the Combined Action of Light and Water in the Liberation of the Perfumes of Plants.—Eugene Mesnard.—It is light, and not oxygen as it has been assumed, which is the principal cause of the transformation and destruction of odorous substances, but in many cases these two agents seem to act in concert. The action of light makes itself felt in two different manners: on the one hand, it acts as a chemical power, capable of furnishing energy to all the transformations through which the odorous products pass from their elaboration to their total resinification; on the other hand, it exerts a mechanical action which plays an important part in the general life-history of plants; and this property explains the mode of the periodical liberation of the perfumes of flowers. The intensity of the perfume of a flower depends on the equilibrium which is established at every hour of the day between the pressure of water in their cellules, which tends to drive outwards the perfumes already elaborated contained in the epidermis, and the action of light which combats this turgescence. The whole physiology of perfumed plants flows from this simple notion. It is thus explained why in the countries of the East the flowers are less odoriferous than with us; why the trees, the fruits, even the vegetables, are sometimes filled with odoriferous products more or less resinified. It is also explained why in those countries the vegetation is thorny: the vegetation in those countries has too much light and too little water.—*Comptes Rendus*, cxxii., p. 493.

MEETINGS FOR THE WEEK.

WEDNESDAY, 8th.—Pharmaceutical, 8.30.

—Astronomical, 8.

FRIDAY, 10th.—Geologists' Association 8.

THE CHEMICAL NEWS.

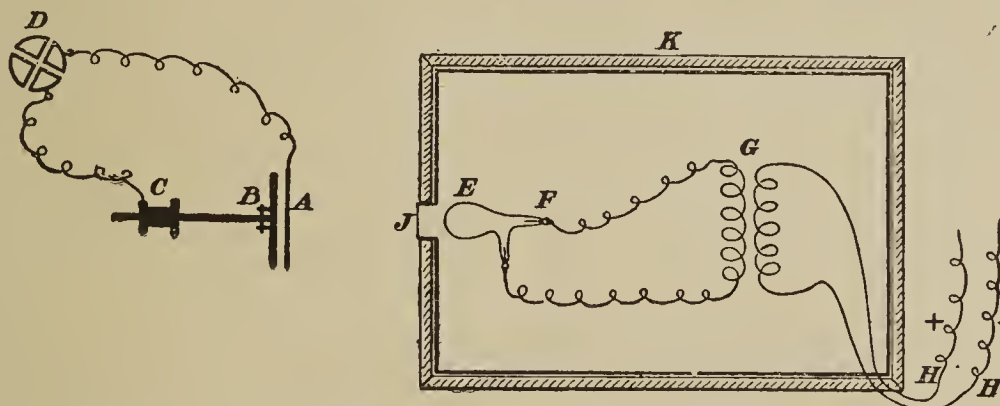
Vol. LXXIII., No. 1898.

ON THE EFFECT OF THE RÖNTGEN X RAYS ON THE CONTACT ELECTRICITY OF METALS.*

By JAMES R. ERSKINE MURRAY, B.Sc.,
1851 Exhibition Scholar, Trinity College, Cambridge.

1. THE experiments described in this communication were made in the Cavendish Laboratory of the University of Cambridge, at Professor J. J. Thomson's suggestion, in order to find whether the contact potential of a pair of plates of different metals is in any way affected by the passage of the Röntgen "X" rays between the plates.

2. The vacuum bulb and induction coil for the production of the rays were enclosed in a box lined with metal, so that the plates and the apparatus used in measuring their contact potential difference should be screened from any direct electrical disturbances. At one



A. Tinfoil plate. B. Zinc plate, supported by a brass rod, which slides through the brass collar, C. D. Quadrant Electrometer. E. Vacuum tube. F. Negative electrode of tube. G. Induction coil. H, H. Wires connecting house battery to induction coil. J. Tinfoil screen—over the hole from which the rays issued—used in some experiments. K. Wooden box lined with sheet zinc.

side of the box there was a circular hole of about 3 c.m. in diameter. The vacuum bulb was placed just inside this hole, and directed so that the rays should stream out through it in a direction perpendicular to the side of the box. In some experiments this hole was closed by a tinfoil screen, which allowed a large proportion of the rays to pass out while shutting in ordinary electrical disturbances. The plates whose contact potential difference was to be measured were placed at a short distance outside the box, in such a position that the rays could fall on them.

3. The diagram given above shows a plan of the principal parts of the apparatus, but omits the insulating supports and the subsidiary apparatus used in determining the contact potential by Lord Kelvin's null method. It is drawn roughly to scale, so as to show the relative dimensions and positions of the various parts.

4. To measure their contact potential I used the null method described by Lord Kelvin in his paper given to the British Association in 1880. I shall not describe this method in detail in the present communication, but may mention that the value of the contact potential is found by measuring the amount of the counter potential which has to be applied to the pair of plates to reduce the potential difference between their opposing surfaces to zero. The counter potential introduced to effect this annulment must obviously be equal and opposite to their contact potential difference.

* A Paper read before the Royal Society.

Hence the numerical value of the latter is simply that of the applied counter potential, but is of opposite sign.

5. The plates were of zinc and tinfoil, the latter being mounted on thin ebonite to keep it flat. They were placed parallel to one another at a small distance apart, so that the rays fell perpendicularly on the back of the tinfoil plate, passed through it and the air space between them, and were absorbed by the zinc. The tinfoil plate was insulated and connected to the insulated quadrants of a Kelvin quadrant electrometer. The zinc was uninsulated, and was connected to the uninsulated quadrants of the electrometer. This plate is movable in a direction perpendicular to its plane, and can thus be drawn away from the tinfoil. If there is any electric potential difference between the opposing surfaces of the two plates, further separation causes a change in it which, reacting on the electrometer, deflects it.

6. When everything was in position, before starting the rays I measured the contact potential of the plates by the method mentioned above, and found it to be—

+0.44 volt,

the zinc being positive to the tinfoil. The rays were now turned on so as to pass through the tinfoil plate on to the zinc. The contact potential, measured while the rays were passing, was about—

+0.43 volt.

But before the plates could be separated to see whether the counter potential applied had annulled the contact potential or not, the charge leaked away as if the insulation of the tinfoil plate were bad. Also I observed that when the plates were not in connection with one another, but only with the electrometer, they seemed to act as though they were connected together by a bad conductor or an electrolyte.

7. The X rays were now turned on so as to pass perpendicularly through the tinfoil plate on to the zinc. In a few minutes the deflection indicated—

—0.50 volt.

and remained steady there for several minutes. While in this condition I separated the plates. The deflection increased by a small amount, showing that the electrolytic power of the air while the rays are passing through it had somewhat more than counterbalanced the contact potential of the plates, and had established a slight difference of potential in the direction opposite to that which exists between the surfaces of the plates when connected metallically in air. This was confirmed by a measurement, made immediately after, by the null method, which gave—

+0.44 volt

for the potential difference between the plates; the rays not being on at the time.

8. In the experiments described above, the rays had fallen perpendicularly on the plates, passing through the

tinfoil (see diagram). I now placed them so that the rays should pass between them in a direction approximately parallel to their surfaces. On breaking the metallic connection between the plates and turning on the rays the electrometer rose to—

—0.39 volt,

and remained steady there. Separating the plates produced no further deflection, which shows that the contact potential difference between the surfaces of the plates has been reduced to zero. This is confirmed by the measurement, made by the null method, of their contact potential which is now—

+0.39 volt.

9. In the above experiment the plates were at about 1 c.m. apart. I now increased the distance between them to 2, then to 5, and then to 10 c.m.; but in spite of the fact that in the last case the rays must have passed almost entirely through the air between the plates without striking on their surfaces, the electrometer always crept up from zero to —0.39 volt in a minute or two, and remained almost steady at that value.

10. In the above experiments there was no screen between the vacuum bulb and the ebonite back of the tinfoil plate. To make sure that none of the effects observed were due to ordinary electrical disturbances, I now placed a piece of tinfoil, in connection with the metal lining of the box containing bulb and coil, over the hole in the box from which the rays issued. With the plates parallel to the rays, and at about 1 c.m. apart, the electrometer rose while the rays were on from zero to —0.39 volt in two minutes, and remained steady there. This shows that the effects above described are due to the new rays, which can pass with ease through tinfoil, and not to the more ordinary forms of electric radiation.

11. In order to find whether these phenomena were strictly comparable with the results which Lord Kelvin had got many years ago by connecting the plates through an electrolyte, I made several experiments in which connection was made by a drop of acidulated water.

Before doing so, however, I measured their potential difference by the null method and found it to be—

+0.57 volt.

This variation from previous determinations is due no doubt to the influence of the atmosphere in tarnishing the plates. It is much less than the changes, due to that cause, which I have often found in other experiments on contact electricity. I now joined the plates by a drop of acidulated water while they were in connection with the electrometer only. The deflection at once rose from zero to—

—0.54 volt.

I now separated the plates, but this did not cause any notable change in the deflection, though it tended slightly in the direction which indicated that the contact potential of the plates had not been quite balanced by the electrolytic action. This is confirmed by the difference between 0.57 and —0.54 given above. After a short while the deflection fell to—

—0.48 volt,

which is nearly the value found previously for untarnished zinc and tinfoil in air, showing that the acidulated water has, in all probability, removed the tarnish, and is now balancing the contact potential between clean surfaces of the metals. The water was now removed, and the contact potential measured by the null method as before. It is still—

+0.57 volt,

for, of course, by far the greater part of the surfaces of the plates is still tarnished as before. In another experiment with a drop of acidulated water between the plates, I found that the contact potential was more than counterbalanced by the electrolytic action. This corresponds to the action of the rays mentioned in section 7.

12. It now occurred to me, that perhaps the electrolytic connection established between the plates when the rays were passing might be through the insulating supports of the tinfoil plate, and not through the air as I had hitherto supposed. To test the truth of this idea, several variations were made in the arrangements, all with a view to place the insulators in such a position that the rays could not reach them. First, I placed a screen of sheet zinc, with a hole in the middle of it, between the tinfoil plate and the hole in the box, from which the rays issue, so that the rays from the negative electrode of the vacuum bulb could fall only on the tinfoil plate and not on its insulating supports. These, by the way, consisted of pieces of good red sealing-wax, and under ordinary conditions, were excellent insulators. When the rays were started the electrometer moved from zero to a position which indicated a difference of potential as great as or greater than any which had been previously observed. This shows that the electrolytic connection had not been at all affected by screening the solid insulators.

This experiment was repeated several times, and in every case the result was the same. Still further confirmation of the aerial nature of the connection was obtained by a great alteration in the length and position of the insulating support. Instead of three short arches of sealing-wax, each made of one stick about 6 inches long, I used one tall one fully 12 inches high; one leg was attached to the wooden framework on which the uninsulated zinc plate was mounted, and the other, which was somewhat longer, held the tinfoil plate. The new insulator was thus one piece, about 24 inches long, of sealing-wax, with the greater part far removed from the rays, instead of six pieces each 3 inches long. A number of experiments were made with this arrangement. In all of them the potential varied under the influence of the rays by an amount similar in direction and magnitude to that previously observed.

13. I have observed that the activity of the vacuum bulb seems to determine, to some extent, the potential difference observed on the electrometer; that is to say, if the rays are very weak and unsteady (as judged by the fluorescence of the vacuum bulb) they do not make the air sufficiently electrolytic to counterbalance the contact potential difference between the surfaces of the plates. Thus, when the bulb is not fluorescing brightly and steadily, one gets results which are uncertain and perplexing. But these appear to give place in all cases to more definite values whenever the rays are strong and steady.

14. The conclusions I have drawn from these experiments are that (1) the influence of the rays on the zinc and tinfoil plates does not cause any direct or sudden change in their contact potential, but that (2) the air through which the rays pass is temporarily converted into an electrolyte, and when in this condition forms a connection between the plates which has the same properties as a drop of acidulated water, namely, it rapidly reduces the potential between the opposing surfaces of the plates to zero, and may even reverse it to a small extent.

It is interesting to note that this electrolytic property was found by Lord Kelvin ("Electrostatics and Magnetism," Art. xxiii., sections 412—414) to be possessed by the fumes from a burning spirit lamp. In both cases its cause is probably the same. It is, no doubt, due to a want of electrical equilibrium among, and a partial dissociation of, the molecules of the gas.

Constitution of Rhodinol.—Ph. Barbier and L. Bouveault.—The oxidation of the rhodinol of roses yields exactly the same results as that of the pelargonium compound. The two alcohols, $C_{10}H_{20}O$, extracted from the oil of pelargonium and from that of roses are identical. Rhodinol is a primary alcohol with an open chain having ethylenic connection.—*Comptes Rendus*, cxxii., No. 11.

ON THE INVISIBLE RADIATIONS EMITTED
BY THE SALTS OF URANIUM.

By HENRI BECQUEREL.

1. *Action on Electrified Bodies.*

IN one of the last sittings of the Academy I announced that the invisible radiations emitted by salts of uranium have the property of discharging electrified bodies. I have continued the study of this phenomenon by means of the electroscope of Hurmuzesqu, and I have been able to establish otherwise than I had previously done, photographically, that the radiations in question traverse various opaque bodies, in particular aluminium and copper. Platinum presents an absorption much more considerable than the two above-mentioned metals.

If we follow the progressive approximation of the gold leaves of the electroscope during the discharge, we observe that for deviations not exceeding 30° the angular variations are very decidedly proportional to the times, so that the speed of the approximation, or the fraction of a degree in which the gold leaves approach each other in a second, may give an idea of the relative intensities of the active radiations. I give here merely the numbers relating to the absorption through a plate of quartz perpendicular to the axis, and having a thickness of 5 m.m. The speeds are expressed in seconds of the arc and in seconds of time.

A lamella of the double uranyl and potassium sulphate placed below the gold leaves dissipates the charge of the electroscope with a speed represented by 22.50. The interposition of the plate of quartz reduced the speed to 5.43. The ratio of the two numbers is 4.15.

I have examined if the radiations emanating from the phosphorescent wall of a Crookes tube were enfeebled by the same plate of quartz in a proportion of the same order of magnitude. A Crookes tube was arranged at the exterior of the electroscope, opposite one of the faces of the lantern, for the glass of which had been substituted a plate of aluminium of 0.12 m.m. in thickness, and in front of this plate was placed a screen of copper with a circular perforation of 15 m.m. in diameter. The radiations through the copper are so much weakened that this effect may be neglected in the present experiment. When the Crookes tube was excited by an induction-coil, the gold leaves of the electroscope approached each other rapidly, —about 1° in 1.4 second, which corresponds to a speed of 257.14 expressed by means of the units adopted above.

When the quartz plate closed the circular aperture, the speed of the collapse of the gold leaves became 163.63, or 15.7 times smaller.

The enfeeblement is nearly four times greater in the second case than in the first, but it is of the same order of magnitude. This is the only point which this experiment manifests. The observation is not contrary to the probable hypothesis which ascribes the difference to the fact that the rays emitted by the uranium salt, and the rays emitted by the tube or by the phosphorescent glass, have not the same wave-lengths; but the different conditions of the two experiments do not enable us to assert this heterogeneity.

The electroscope has also enabled us to show the slight difference between the emission from a lamella of a uranium salt, which had been kept in the dark for eleven days, and the emission from the same lamella after it has been brightly illuminated with the magnesium light. In the former case the collapse of the leaves had a speed of 20.69, and after the luminous excitation it became 23.08.

We are ignorant what becomes of the electric charges thus dissipated, as also if the dielectrics were rendered conductors whilst traversed by these radiations. Experiment has shown that the crystalline lamella, if properly insulated, does not become charged even though it discharges the electrometer. Further, a lamella placed for a long time in presence of the apparatus does not communicate to it any charge.

2. *Emission of different Uranium Salts. Permanence. Excitation.*

If the phenomenon of the emission of invisible radiations which we have studied is a phenomenon of phosphorescence, we should be able to show the excitement by given radiations. This study is rendered very difficult by the prodigious permanence of the emission when the substances are kept in the dark secluded from luminous radiations, or from invisible radiations the nature of which we know. After more than fifteen days the salts of uranium still emit radiations almost as intense as on the first day. If we place on one and the same photographic plate, across black paper, a lamina which has been kept for a long time in the dark, and another which has just been exposed to the light of day, the impression of the silhouette of the second is a little stronger than that of the former. The magnesium light in these conditions produces merely an inappreciable effect. If we brightly illuminate the laminae of the double uranyl and potassium sulphate with the electric arc, or with the brilliant sparks from the discharge of a Leyden jar, the impressions are decidedly blacker. The phenomenon seems therefore to be a case of invisible phosphorescence, but which does not seem to be intimately mixed with visible phosphorescence or fluorescence. If, in fact, the uranium sesqui-salts are very fluorescent, it is known that the green uranous salts (the curious absorbent properties of which I have had the opportunity of studying) are neither phosphorescent nor fluorescent. But uranous sulphate behaves like uranic sulphate, and emits radiation as intense.

I will still mention another interesting experiment. We know that uranium nitrate ceases to be phosphorescent or fluorescent when it is in solution or melted in its water of crystallisation. I took a crystal of this salt, and after having placed it in a small tube closed with a thin plate of glass, I heated it in the dark, so as to avoid even the radiations of the alcohol lamp which supplied the heat. The salt was melted, and then allowed to crystallise in darkness, and I then placed it on a photographic plate covered with black paper, so as to preserve always the salt from the action of light. We might expect to observe no action, all luminous excitement having been avoided from the moment when the substance ceased to be phosphorescent, and yet the impression was as strong as that of salts exposed to the light, and even at points where the salt adheres to the plate of glass the impression was stronger than that of a specimen of uranium sulphate used for a comparative experiment on the same plate.

On this same photographic plate there were also crystals of uranium nitrate resting on laminae of glass with different surfaces, but the effects were sensibly the same.

I have also arranged uniform surfaces, formed of uranium sulphate and of double uranium-potassium sulphate, and I projected on these surfaces the spectrum of the arc through an apparatus of quartz. The bands of ultra-violet excitement were shown very definitely by fluorescence; but when I reproduced the silhouette of these surfaces upon a photographic plate, the silhouette became almost uniformly black, showing either that the specific emission of the substances marked the slight differences which might be observed for the different regions of excitation, or that the excitation did not take place in the region of the spectrum which was projected upon the surface studied.

3. *Absorption of different Substances.*

We may very easily study qualitatively the absorption of the radiation in question, by arranging on one and the same photographic plate sheets of these substances, or small flat tubes full of liquids, and covering them with a lamina of the double uranium-potassium sulphate, or any other uranium salt.

With these various substances used, in thickness

differing little from 2 m.m., I found that water is very transparent; the majority of the solutions, even those of metallic salts, solutions of copper nitrate, gold chloride, uranium nitrate, an alcoholic solution of chlorophyll proved moderately transparent. It was the same with paraffin and modeller's wax. Uranium glass was more opaque, as also a glass coloured red. Aluminium of this thickness is sparingly transparent; tin is more opaque, and a cobalt-blue glass appeared more opaque than the foregoing metals.

In another series of experiments I arranged different crystals and different optical combinations, intended to manifest the phenomena of double refraction and of polarisation. The images obtained were so feeble that I cannot at present give the results; still it was perceptible that quartz absorbs these invisible radiations more than does Iceland spar. Native sulphur behaved as if transparent.

The experiments in air and in rarefied air, which I mentioned at the end of my last paper, though not showing very signal differences, showed that proofs in rarefied air are a little stronger, which would manifest an absorption of air.

4. Refraction.

The facts which I mentioned in my last memoir have manifested refraction through glass. To these experiments we may add the following:—On one of the faces of a prism of crown glass, at a few m.m. from the edge, we fix, parallel to the latter, a small tube of very thin glass, of about 1 m.m. in diameter filled with crystallised uranium nitrate, and forming a linear source of emission of invisible radiations.

We then apply the other surface of the prism on a photographic plate. On developing the plate three days afterwards there was observed a diffused impression under the base of the prism; an impression separated from the trace of the edge by a white line, and the displacement of which is of the order of magnitude of that obtained under the same conditions for light. The considerable diminution of the luminous intensity when the sources of light are removed a little from the photographic plate has not allowed me hitherto to make measurements of the indices of refraction.

5. Anomalies presented by Different Substances.

The uranium salts emit invisible radiations with a remarkable permanency, but it is not the same with other phosphorescent substances.

I have obtained with calcium sulphide results of the order of those given by the salts of uranium, and I have mentioned in my last paper a proof of remarkable intensity obtained through 2 m.m. of aluminium. The same phosphorescent matter placed on a second photographic plate, under the same conditions, showed itself inactive, and since then I have not succeeded in obtaining any image with calcium sulphides. I have had the same want of success with specimens of hexagonal blende from different sources. I then sought to communicate a new activity to those substances by various known procedures, I have heated them in presence of the photographic plate without heating the latter, but I have not been able to obtain any impression.

In another series of experiments the various substances were refrigerated down to 20°, excited by daylight and by the magnesium light, but the magnesium salts alone yielded images.

Lastly, I have excited sulphides and hexagonal blende by the sparks from the discharge of a battery, and the substances, though rendered highly phosphorescent, still did not manifest any action through black paper. I have learned in the course of these experiments that our eminent colleague, M. Troost, has observed an analogous fact. Very old specimens of hexagonal blende which had at first yielded him energetic results have subsequently yielded results progressively decreasing, and are then

become inactive. There is here a very curious fact which may perhaps be explained by ulterior experiments.

M. L. Troost added the following observation on the foregoing paper:—

Our colleague, M. Becquerel, has observed that phosphorescent calcium sulphide, which in his earlier experiments acted very vividly on a silver gelatino-bromide plate, suddenly lost all its activity.

I have observed an analogous phenomenon with artificial hexagonal blende prepared by the apparent volatilisation of zinc sulphide in a very slow current of pure and dry hydrogen at a very high temperature.

This blende, the phosphorescence of which has been repeatedly excited by the magnesium flame, after having given for some time good proofs, produced afterwards paler and paler proofs, and finally nothing at all.

A new specimen, recently prepared, acted effectively under the conditions of my former experiments. On continuing this study I am about to verify if this activity will maintain itself or if it will disappear as in the former case.—*Comptes Rendus*, cxxii., p. 689.

THE STRUCTURE AND CONSTITUTION OF ALLOYS OF COPPER AND ZINC.

By GEORGES CHARPY.

In a paper submitted to the Academy in 1893, we indicated that the microscopic examination of the structure of brass may permit us to follow the modifications produced in this metal by treatment mechanical or chemical. Since that date we have examined in the same manner a great number of alloys of copper and zinc of various compositions and subjected to different treatments. The sum of these researches leads to the following conclusions:—

1. The alloys containing from 0 to 35 per cent of zinc all contain the same micrographic characters; the metal obtained by casting is formed by the agglomeration of long dendritic needles, the ramifications of which are often at right-angles. The dimensions of these crystallites depend chiefly on the speed of solidification of the metal. If we keep the metal at a temperature, high but below the point of fusion, the crystals develop, become more distinct, and finally pervade all the mass. They are then octahedra, presenting numerous macles, the dimensions of which are so much the greater as the metal has been raised to a higher temperature. We have not been able hitherto to effect the measurement of the angles of these crystals, but they seem to have identically the same form, and to constitute the totality of the mass as well in copper as in the alloy with 34 per cent of zinc, and all the intermediate alloys, which leads us to consider all these metals formed of isomorphous mixtures. For this group of metals there are hence two very definite structures; the one with dendritic crystals corresponds to fused metals; the other formed of very definite octahedral crystals corresponds to the state of perfect tempering. All cold hammering is recognised by the existence of deformed crystals, and all imperfect tempering by the appearance of small and ill-developed crystals.

When the proportion of zinc exceeds 34 per cent, the structure of the metal changes; the melted metal is formed of crystallites with rounded borders, and without dendritic ramifications; this structure is not appreciably developed by re-heating, and whatever may be the treatment undergone by the metal we have always two different substances—crystals entangled in a paste. When the proportion of zinc augments, these crystals become more rare, above 45 per cent the metal is formed of large plates with polygonal outlines which seem to have been developed around a certain number of centres of solidification, and in the interior of which we distinguish small crystals. When the proportion of zinc reaches 67 per cent, we have an alloy with a conchoidal fracture, and

which seems apparently homogeneous; but when the proportion of zinc becomes greater, potassa dissolves certain portions and shows ill-formed crystals which seem entangled in the zinc.

2. The observations relating to the microscopic structure enable us to interpret certain facts concerning the mechanical properties. In the alloys with a distinctly crystalline structure (from 0 to 34 per cent of zinc) the impurities are localised among the crystals. In the brasses of industry these impurities—which are almost always weak metals, lead or tin—form a solder which in the cold presents a great resistance. We find, in fact, that the malformations and the fractures are produced in the interior of the crystals, which explains why the fracture of these alloys formed of large crystals presents a very fine grain. But if we raise the temperature, the resistance of the solder decreases rapidly, and on passing 200° the metals become very fragile, the rupture taking place between the surfaces of the crystals. When the proportion of zinc is about 40 per cent, this effect is not produced; the crystals never occupy all the mass, and the impurities being distributed in a considerable mass do not weaken it so rapidly. It is known, in fact, that brasses containing from 36 to 45 per cent of zinc can be forged in heat.

3. The physical properties of the alloys of copper and zinc indicate plainly the existence of a definite compound, CuZn_2 (67.3 per cent of zinc), which has been isolated by Le Chatelier. The researches of M. Riche on densities indicate likewise a perturbation in the neighbourhood of the alloy Cu_2Zn (34.5 per cent of zinc). On comparing these results with those furnished by microscopic study, we are led to put forward the following hypotheses on the constitution of the alloys of copper and zinc; alloys containing from 34.5 to 67.3 per cent of zinc must be mixtures in variable proportions of Cu_2Zn (a malleable compound) and of CuZn_2 (a hard, brittle compound) approximating more or less, according to their composition, to the properties of the one or the other definite alloy. Lastly, the alloys containing more than 67.3 per cent of zinc will be mixtures of zinc with the compound CuZn_2 .—*Comptes Rendus*, cxxii., p. 670.

APPROXIMATE DETERMINATION OF THE VALUE OF CRUDE CRESOL.

By A. SCHNEIDER.

THE author founds his process upon a comparison of the intensity of the yellow colour assumed respectively by a pure cresol mixture and by cresols obtained from the substance under examination on treatment with nitric acid and ammonia. He first prepares a pure cresol mixture by dissolving crude cresol in soda-lye, diluting the solution with 5 vols. of water; the hydrocarbons (naphthalene, &c.) are removed by shaking out with benzene, and the cresols are separated by means of acid, the pyridines being combined at the same time. The cresols eliminated are collected, dried with calcium chloride, and distilled. Or we may use commercial cresol dehydrated by means of calcium chloride.

Of this pure cresol, 1 grm. is dissolved in water, and the solution is made up to 100 c.c. This solution serves as a standard for comparison.

One grm. of the cresol under examination is also dissolved to 100 c.c.; a knife-point full of powdered quicklime is added in order to seize upon any resinous matters which may be separated, and to increase the solubility of the cresols inclosed by the insoluble matters. We then take 1 c.c. of the solution of the crude cresol = 0.01 grm. of the substance, add 5 c.c. of dilute nitric acid, and heat on the water-bath for five minutes. The yellow liquid is then poured into a glass cylinder suitable for colorimetric comparisons, the rinsings are added, as also 10 c.c. of liquid ammonia, and the cylinder is filled up with water.

0.85 c.c. of the solution of the pure cresol (= 0.0085 grm. of pure cresol) are treated in the same manner, and the colours of the two solutions are compared. Of an official sample, the colour of 0.01 grm. crude cresol should not be weaker than that of 0.0085 grm. pure cresol.

The author assumes as the lowest percentage of an official sample 85 per cent of pure cresol, since cresols can take up as much as 12 per cent of water, and we may calculate on 3 per cent of other impurities. A high percentage of water is shown by the circumstance that such samples give with benzene a turbid mixture, whilst anhydrous samples form a clear mixture therewith.—*Zeitschrift Analytische Chemie*, xxxv., p. 115, and *Pharm. Central Halle*.

ANALYSIS OF A MIXTURE OF CHLORIDES, CHLORATES, AND PERCHLORATES.

By AD. CARNOT.

THE products of the ignition of chlorates may contain chlorates, perchlorates, and chlorides; they may contain hypochlorites. On the other hand, the products formed in the cold, or by the moist way, bleaching chlorides and hypochlorites, never contain perchlorates.

The examination of these two sorts of products constitute, therefore, two problems perfectly distinct in practice.

I shall here indicate the method for the analysis of the products of the dry way, mixtures of chlorides, chlorates, and perchlorates.

I first satisfied myself that the perchlorates do not undergo any reduction on the part of the reagents of the moist way which so readily transform the chlorates into chlorides, especially ferrous sulphate mentioned in a former paper, sulphuric acid, or zinc in presence of acids.

We may further effect the determination of the chlorate and of the chloride by one of the two following methods (A and B):—

A. We take two equal parts of the solution; in one we make directly the volumetric determination of the chloride, after the addition of nitric acid and of ferric sulphate, by means of an excess of silver nitrate and ammonium sulphocyanide; in the other, we effect the reduction of the chlorate by ferrous sulphate, and then continue, in the same liquid, to determine total chlorine. The first operation gives the chlorine of the chloride, and the second, by difference, the chlorine of the chlorate.

B. We operate upon one and the same portion of the liquid to be analysed. We determine the chloride by means of a standard solution of silver nitrate poured into the neutral liquid, after having added, as an indicator, a little sodium or potassium arseniate (in preference to potassium chromate, which has the inconvenience of acting on the reducing agent subsequently employed). Then we determine the chlorate by an addition of sulphurous acid and of ferrous sulphate in a known quantity, as directed in the former memoir. We may then calculate the chlorine of the chlorate and that of the chloride.

As for the perchlorate, it is determined by a special operation, and to that end it is reduced to the state of chloride in the dry way, since the moist way does not succeed.

It is difficult to obtain the complete reduction of the perchlorate in a crucible or in a glass tube without loss by volatilisation, although these procedures have been recommended. If we operate in a platinum crucible we observe a notable deficiency. If we make use of a test-tube we may judge from the white sublimate deposited at the mouth of the tube that there is great danger of loss. The melted chloride, besides, does not dissolve very readily.

But we may avoid all difficulty by a very simple expedient, which consists in mixing the saline powder to be

analysed with four or five times its weight of pure quartz sand, very fine, well washed, and dried.

We introduce the mixture at the bottom of a platinum crucible, and pour upon it sand enough to occupy a depth of 1 or 2 c.m. in the crucible, according to the quantity of matter to be treated. Experience shows that a depth of the layer of sand of 0.25 or even 0.5 c.m. does not entirely prevent all loss by volatilisation if we operate upon 0.500 grm. or 1 grm. of matter.

We heat over the Bunsen burner for twenty to thirty minutes, so that merely the bottom of the crucible is heated to redness. The chlorate and the perchlorate are thus entirely reduced, and if any chloride is volatilised it is condensed immediately on penetrating into the cooler and less permeable stratum of sand, the base of which is sometimes agglutinated for a thickness of several millimetres.

On treatment with water, all the chloride is dissolved in a few seconds. We filter and wash the sand with the greatest ease. Finally, in the neutral solution we determine the chlorine with a standard solution of silver nitrate, in presence of an alkaline chromate or arseniate.

This determination shows the proportion of *total chlorine*. That of the perchlorate is calculated by difference, deducting the proportion of the chlorate and the chloride, already ascertained by the foregoing experiments.

Five check experiments showed discrepancies of less than 0.5 m.grm.—*Comptes Rendus*, cxxii., p. 452.

ON A

NEW ELEMENT PRESENT IN THE RARE EARTHS CONTIGUOUS TO SAMARIUM.

By EUG. DEMARÇAY.

It is well known that Marignac obtained, by fractionating, earths contiguous to samarium, having sparingly soluble potassium sulphates, an earth which he named at first *Ya*, and then gadolinium, after Lecoq de Boisbaudran had characterised it more definitely by its peculiar spectrum. On fractionating by crystallisation from fuming nitric acid (sp. gr. = 1.45) the portion of the rare earths rich in samarium, I separated at first a colourless nitrate, sparingly soluble in the cold, and giving only feeble traces of the absorption-bands of samarium, and showing with the spark a very fine and rich spectrum of gadolinium, then more soluble fractions, becoming more and more yellow up to portions of an orange-yellow, and very intense.

These latter afford a fine line spectrum, without any traces of the rays or the bands of gadolinium. If we examine the inner fractions with the spark, we see the strong rays of gadolinium become weaker in proportion as the nitrates become more soluble, and, inversely, the very feeble rays of samarium become stronger.

But along with the latter there are others of a medium intensity in the first spectrum, which are strengthened at first so as to reach their maximum lustre, whilst the rays of gadolinium are enfeebled, and those of samarium are not yet very strong, and diminish further in intensity until they appear only very faintly in the purest samarium which I possess as yet.

We are therefore obliged to admit the presence of a peculiar nitrate, more soluble in strong nitric acid than that of gadolinium, and less than that of samarium. The earth obtained from this nitrate differs from the rare earths already known:—

1. By its colourless salts without an absorption spectrum.
2. It is colourless, which distinguishes it from terbia.
3. It differs by its spectrum from the oxides of lanthanum, cerium, gadolinium, ytterbium, and terbiu, the only rare earths yet known with colourless salts.

It is, further, very distinct from the oxides of lanthanum and cerium by its relatively feeble basicity and the relative solubility of its double potassium sulphate; from ytterbia, by its relatively strong basicity and the slight solubility of its double sulphate; but it approximates much to gadolinia and samaria, from which it is distinguished by its spectrum. I shall designate provisionally, until I have succeeded in isolating it in a greater state of purity, the radicle of this earth as Σ , and the earth itself as Σ_2O_3 .

Besides Σ_2O_3 we may suspect the presence of another earth. If, in fact, we carefully compare the spectra of gadolinium and of Σ , we find the rays of the former stronger in the first spectrum than in the second; there are others approximately as strong in the one as in the other, and which may belong to a third element. I do not wish to insist on this doubtful point, which particular circumstances may explain otherwise, and I content myself with mentioning some strong rays which seem to me to belong respectively to gadolinium and to Σ . Among the rays of the latter I mention, as the most characteristic, 4228.1, 4205.9, 4128.4, 3972.2, 3930.8, 3819.9; among those of gadolinium we remark, especially, 4263.1, 4178.2, 4098.6, 4063.4, 4049.9, 3959.9, 3958.1, 3916.7, 3852.6, 3850.9, 3549.3, 3545.7.

I have been able to satisfy myself, thanks to the kindness of Lecoq de Boisbaudran, that none of the foregoing rays can be ascribed to terbiu. He has kindly placed at my disposal a specimen of his purest gadolinia, the result of prolonged fractionations of Marignac's sample (already very rich); on the other hand, a terbia of a very deep chocolate-brown, the fruit of beautiful researches, which have led among other discoveries to that of dysprosium. I have examined their spectrum, and found that Σ only occurs there incidentally.

I am indebted to the same *savant* for the opportunity of having been able to examine a samaria prepared by Prof. Clève, and which is considered as one of the purest hitherto obtained. The earth of the illustrious Swedish *savant* contained no terbia, and little gadolinia, but it should contain a considerable proportion of Σ . Hence I conclude that the atomic weight of samarium should certainly be changed, and probably reduced below 150, the figure now received.—*Comptes Rendus*, cxxii., p. 728.

THE COMPOSITION OF WATER. A SHORT BIBLIOGRAPHY.

By T. C. WARRINGTON, B.A.

(Continued from p. 157).

C. Combination of a Weighed Quantity of Hydrogen with Oxygen to form a Weighed Quantity of Water.

(41). 1870. JULIUS THOMSEN.

"Ueber einige Constanten des Wasserstoffs und des Sauerstoffs."

Ber., (1870), iii., p. 927.

A short account of one experiment is given.

(42). 1886. J. D. VAN DER PLAATS.

"Essai de Calcul des Poids Atomiques de M. Stas."

Ann. Chim. et Phys., (1886), [6], vii., p. 499.

In a note on p. 529 of the paper is given the result of one experiment by the author. On the same page is discussed the value for H (O=16) from Stas's determination of molecular weight of NH_4Cl and NH_4Br .

(43). 1887. E. H. KEISER.

"Ueber die Verbrennung abgewogener Mengen von Wasserstoff und über das Atomgewicht des Sauerstoffs."

Ber., (1887), xx., p. 2323.
Abs. J. C. S., (1887), lii., p. 1078.
Beibl. Wied. Ann., (1887), xi., p. 743.

Preliminary notice.

(44). 1888. COOKE and RICHARDS.

"The Relative Values of the Atomic Weights of Hydrogen and Oxygen."

Amer. Chem. J., (1888), x., p. 81.
Proc. Amer. Acad., (1888), xxiii., [N.S. xv.], p. 149.
Abs. J. C. S., (1888), liv., p. 647.
Beibl. Wied. Ann., (1888), xii., p. 411.

The paper discusses bearing of Prout's hypothesis, and gives a critical account of previous work. The special feature of the author's procedure is that hydrogen is weighed in a large globe and driven over copper oxide by nitrogen, the ratio $H_2 : H_2O$ being thus obtained.

(45). 1888. COOKE and RICHARDS.

"Additional Note on the Relative Values of the Atomic Weights of Hydrogen and Oxygen."

Amer. Chem. J. (1888), x., p. 191.
Proc. Amer. Acad., (1888), xxiii., p. 182.
Abs. J. C. S., (1889), lvi., p. 910.
Beibl. Wied. Ann., (1888), xii., p. 732.

The object of the note is to apply a correction for the shrinkage of the balloon suggested by Rayleigh's works.

(46). 1888. E. H. KEISER.

"On the Combustion of Weighed Quantities of Hydrogen and the Atomic Weight of Oxygen."

Amer. Chem. J., (1888), x., p. 249.
Beibl. Wied. Ann., (1888), xii., p. 733.

Palladium was used to condense and weigh hydrogen, which was then passed over heated copper oxide and the water weighed.

(47). 1889. W. A. NOYES.

"On the Atomic Weight of Oxygen."

Amer. Chem. J., (1889), xi., p. 155.
Chem. News, (1889), lix., p. 244.
Abs. J. C. S., (1889), lvi., p. 672.
Beibl. Wied. Ann., (1889), xiii., p. 585.

Hydrogen is led into an apparatus containing a weighed amount of hot copper oxide. The increase in weight gives the weight of hydrogen. The apparatus is then exhausted of water and again weighed to obtain the weight of water formed.

(48). 1889. G. STILLINGFLEET JOHNSON.

"Note on the Method of Determining the Atomic Weight of Oxygen adopted by W. A. Noyes."

Chem. News, (1889), lix., p. 272.
Abs. J. C. S., (1889), lvi., p. 935.
Beibl. Wied. Ann., (1889), xiii., p. 842.

The errors from occlusion, the presence of sulphur in copper, &c., pointed out.

(49). 1890. W. A. NOYES.

"The Atomic Weight of Oxygen."

Amer. Chem. J., (1890), xii., p. 441.
Proc. Amer. Ass., (1890), xxxix., p. 167.
Abs. J. C. S., (1890), lviii., p. 1370.
Nature, (1890), xlii., p. 530.

The author corrects and extends his former results.

(50). 1891. W. A. NOYES.

"The Atomic Weight of Oxygen."

Amer. Chem. J., (1891), xiii., p. 354.
Abs. J. C. S., (1891), lx., p. 1154.

The paper consists of a rejoinder to Keiser (29).

(D). Indirectly from the Molecular Weight of Ammonium Chloride.

(51). 1860-1882. J. S. STAS.

"Recherches sur les Rapports réciproques des Poids Atomiques."

Bull. de l'Acad. Belgique, (1860), x., p. 294.

"Nouvelles Recherches sur les Lois des Proportions Chimiques."

Mém. de l'Acad. Belgique, (1865), xxxv., pp. 48-58.

"Du Rapport Proportionnel entre l'Argent, les Chlorures, et les Bromures."

Mém. de l'Acad. Belgique, (1882), xliii., p. 62.

Stas determines the relation of Ag to NH_4Cl and NH_4Br , and so the molecular weight of these substances. Then the molecular weights of nitrogen, chlorine, and bromine being otherwise accurately determined, the atomic weight of hydrogen, compared with $O = 16$, can be found.

(52). 1894. J. THOMSEN.

"Experimentelle Untersuchungen zur Feststellung des Verhältnisses zwischen den Atomgewichten des Sauerstoffs und Wasserstoffs."

Zeit. Phys. Chem., (1894), xiii., p. 398.

Beibl. Wied. Ann., (1894), xviii., p. 809.

The author finds the quantity of ammonia gas requisite to saturate a given weight of hydrochloric acid. Then atomic weights of nitrogen and chlorine being known, the atomic weight of hydrogen ($O = 16$) may be calculated.

(53). 1894. MEYER and SEUBERT.

"Ueber das Verhältniss der Atomgewichte des Wasserstoffs und des Sauerstoffs."

Ber., (1894), xxvii., p. 2770.

Beibl. Wied. Ann., (1895), xix., p. 226.

Criticism of J. Thomsen's method (51).

(To be continued.)

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 161).

CHAPTER X.

THE CHARACTERS IMPARTED TO FLAMES AND TO THE ELECTRIC SPARK DISCHARGE AND ARC BY BARIUM COMPOUNDS.

The Luminous Spectra of Barium.—Compounds of barium impart to colourless flames, and to electric sparks and discharges, a greenish yellow tint. The green tint is stronger when the compounds are free from sodium. An electric arc charged with baryta is *white*. Spectrum analysis of flames charged with baryta shows a spectrum with very numerous and varied bands. I did not like to acknowledge myself beaten, considering the question I was investigating, viz., whether, by increasing the temperature of flames or the intensity of electric phenomena, it was possible to cause the appearance of lines characteristic of sodium, potassium, lithium, calcium, or strontium, when the compounds of barium were previously freed, by means of chemical and physical forces, from the slightest trace of these metals.

For carrying on this investigation I employed sulphate of barium made by two different processes, sulphide made from these sulphates, and oxide made in an oxyhydrogen blowpipe from carbonate and chloride of barium prepared from sulphide.

In the last chapter I described in detail the methods by which I prepared these compounds.

No matter what the source of the barium might be, its spectrum, in an oxyhydrogen blowpipe at the highest possible temperature, was always the same.

When it was derived from sulphate prepared by either method, but in a medium free from *silica* and as much as possible from sodium, as is the case with chloride crystallised ten times in succession in platinum, and then heated several times in platinum to a dull red heat with chloride of ammonium, and taken up each time in pure water, I found the following facts:—

Sulphate, when dried protected from air dust, and heated on a sheet of platinum free from sodium, immediately coloured *pure yellow* an oxyhydrogen blowpipe burning with a large excess of hydrogen. On regulating the temperature so as to dry the sulphate only without fusing it, it was noticed that after a short time the yellow colour disappeared from the blowpipe, and was replaced by a pale greenish yellow at first, and afterwards by a *deep green* colour. After having sufficiently renewed the layers of simply dried sulphate, spectrum analysis of the flame showed that the sodium line gradually faded, until it reached the state in which it was seen in a blowpipe burning in the surrounding air.

By taking great care, it is possible to bring the sulphate to a condition in which it no longer shows traces of the sodium line, even before it is heated enough to melt it in small *clear, transparent, and colourless* drops, which remain on the surface of the dried sulphate like dew, having the appearance, on cooling, of white enamel.

I succeeded, on several occasions, in eliminating the sodium which is firmly held by the sulphate, and using salt from two different sources, and I got the best result when separating, as I did the night before with carbonate of strontium, nearly all the sodium, and then completing the reaction in a carefully washed room and in still air.

When two persons are engaged in carrying on this delicate work,—one being engaged in volatilising the compound by suitably adjusting the blowpipe, and the other in examining the spectrum formed,—one is very soon convinced that there is no connection between the sodium line and the yellow barium lines, in spite of their proximity when a spectroscopic of low dispersive power is used. When the precaution is taken of volatilising at least *two-thirds* of the sulphate experimented upon, no matter what the temperature of the sulphate, or rather the products of its dissociation, may be, and when a Duboscq spectroscopic with three prisms is used, it is impossible to cause the appearance of a line corresponding to either *one or other of the double sodium line in the solar spectrum taken as a standard*.

It is impossible to produce a trace of sodium from sulphate of barium by raising the temperature.

There can be no possible doubt on this point. As regards the spectrum of sulphate of barium, and the products of its dissociation, my observations have yielded the following results:—

The Flame Spectrum of Sulphate of Barium.—Sulphate, when entirely freed from sodium and heated in an oxyhydrogen blowpipe to a temperature below that at which the diffuse greenish line, at 82.2 on the Steinheil and 90 on the Bunsen spectroscopic, appears, shows a spectrum consisting entirely of the red, orange, and green bands, made familiar to us by Bunsen's and Kirchhoff's work. When the temperature is high enough to show the greenish blue line, the bands show a tendency to better definition, but I cannot say that I have succeeded in seeing a single sharp line in the spectrum, not even the greenish blue line above mentioned.

The position of the bands was *remarkably constant*; I ascertained the position to be the same as described by Bunsen, in his "Spectral Analytische Untersuchungen," for the flame spectrum of chloride of barium, within the limits of error of measurement, *i. e.*, 0.50 division on the micrometer.

On raising the temperature, so as to colour the oxyhydrogen flame quite blue with incandescent hydrogen, the appearance of the spectrum changes and it becomes intensely brilliant. The bands at 59.75 to 61.80, and 85.2 on the Steinheil spectroscopic, corresponding to 61 to 63, and 90 on the Bunsen spectroscopic, tend to resolve into lines; they still, however, remain hazy. In the middle of the interval between *E_b* and *F*, there appears a band which, at the point of greatest brilliancy, is seen to consist of a *group* of extremely fine *green lines*. These green lines, the number of which varies with the temperature, occupy six and a half divisions on the micrometer; they are situated between 75.5 and 82 on the Steinheil spectroscopic, corresponding to from 79 to 86 on the Bunsen scale. This complex group is drawn on the accurate illustration of the flame spectrum of chloride of barium given by Roscoe. When using the Duboscq instrument with three flint glass prisms, I tried to determine accurately the position of each of these lines, but did not succeed. The absorption of light was so great that I could only just see the lines.

I tried again with the Hilger instrument with three Iceland spar prisms, but with no better success.

Whatever the reason may be, the appearance of the spectrum of sulphate of barium, and the products of its dissociation, varies, according as it is examined in the part of the oxyhydrogen blowpipe where the hydrogen is or is not incandescent. In the first case the spectrum drawn by Roscoe, in the second case that described by Bunsen, is seen. But in neither case is there seen any trace of the characteristic spectra of potassium, lithium, calcium, or strontium.

As regards calcium and strontium, I specially directed my attention to finding out whether, *during* or *after* the dissociation of the sulphate and when the temperature was at its highest (the fusing-point of iridium), the appearance of the spectrum changed, and especially whether the blue calcium line at 125.5 and the blue strontium line at 99.0 on the Steinheil spectroscopic, corresponding to 135.0 and from 105 to 106 on the Bunsen instrument, appeared even momentarily, as I found they did when I purposely mixed with the sulphate of barium about 1/10,000th part of the sulphates of calcium and strontium.

I was not able to detect the blue calcium and strontium lines. I call special attention to the blue calcium line at 125.5 on the Steinheil spectroscopic, and not the green calcium band from 60 to 61.5, because the flame spectrum of sulphate of barium, when quite free from sulphate of calcium, has a *green line at the same place when measured in the Steinheil spectroscopic*. When using the large Hilger instead of the Steinheil spectroscopic, it is readily seen that there is, between the green barium and the green calcium lines, a distance equal to about *three times* the width of the lines. The coincidence in the position of the green barium and calcium lines, noted by spectroscopists, must be due to a want of dispersive power in the instruments used by those observers. My numerous researches, at different times, to satisfy myself as to the purity of sulphate of barium, have led me several times to undertake the spectrum analysis of an oxyhydrogen blowpipe charged with this compound, both at the lowest and highest possible temperatures, and the results have always been the same when I had succeeded in previously eliminating the calcium and strontium so firmly combined with barium.

The Flame Spectrum of Sulphide of Barium.—As I described in the last chapter, I converted pure sulphate of barium, free from sodium, into sulphide, both by means of hydrogen in platinum, and by means of petroleum black, in a pure carbon crucible.

The sulphide made by means of hydrogen in platinum, when volatilised in oxyhydrogen gas with an excess of hydrogen, showed on spectrum analysis, at corresponding temperatures, the same spectra as those of pure sulphate in an oxyhydrogen flame. The bands in these spectra are as constant in position as those of the sulphate.

Moreover, I found analytically that, in an oxyhydrogen blowpipe with an excess of hydrogen, the sulphide of barium was quickly reduced to the form of a mixture of oxide and sulphate of barium.

The Flame Spectrum of Chloride made from Sulphide of Barium.—After having reduced the sulphate free from sodium in platinum, by means of hydrogen, I transformed the resulting sulphide into chloride. This reaction was effected, protected from draughts, by means of the very purest hydrochloric acid, and without withdrawing the platinum boat containing the sulphide from the porcelain tube. The chloride thus formed, when heated at once in an oxyhydrogen blowpipe with an excess of hydrogen, showed, at a temperature below that of incandescent hydrogen, the barium spectrum with the well-known *nebulous* bands, and, at a temperature approaching the fusing-point of iridium, after transforming the chloride into oxide, a spectrum composed solely of well-defined bands, but without lines properly so-called, not even the line at $82\cdot2$ on the Steinheil, or go on the Bunsen, spectroscop.

I saw a very faint sodium line at the commencement of the heating; but long before the chloride was transformed into oxide, I was not able to see the sodium line any more distinctly than in air at the same time.

The Flame Spectrum of Carbonate of Barium.—Wishing to study the flame spectrum of carbonate of barium, and of the oxide made from it, I prepared some carbonate from pure chloride, as described in the last chapter.

Although I mentioned at some length, in the last chapter, the necessity for effecting the precipitation of chloride by means of sesqui-carbonate of ammonium in platinum, as well as all the washings of carbonate of barium, and of entirely avoiding the use of glass, I think I ought to emphasize the point, so as to leave no doubt whatever to anyone who may attempt this operation in glass vessels. By neglecting this precaution, silica, calcium, and sodium from the glass are introduced, and the resulting carbonate of barium—when introduced into an oxyhydrogen blowpipe in which the hydrogen is incandescent—shows, on spectrum analysis, a permanent sodium line, and even the blue calcium line at 135 on the Bunsen spectroscop.

The results of these observations on carbonate of barium apply therefore to a salt prepared exclusively in platinum.

Carbonate made and kept protected from air dust, when heated in an oxyhydrogen blowpipe, gave it a very fleeting yellow colour. When the temperature was raised to bright red, and the layers of the salt were properly renewed, the sodium spectrum disappeared long before the decarbonisation was effected. This result being attained, the barium spectrum appeared with or without a faint sodium line, according to the state of the air. At a similar, but comparatively low, temperature, carbonate imparted to an oxyhydrogen blowpipe a paler green colour than that imparted by sulphate of barium: the spectrum of carbonate was also fainter and less distinct than that of sulphate; it consisted, like the latter, entirely of bands. At the fusing-point of platinum the bands became sharper, but did not resolve into lines. When the fusing-point of iridium was approached, the original bands were still seen, but the band from $75\cdot5$ to 82 on the Steinheil, or from 79 to 86 on the Bunsen, spectroscop, was resolved into the group of *very fine* green lines which I mentioned above in connection with the spectrum of sulphate and the products of its dissociation. Moreover, at this high temperature carbonate ought to be entirely dissociated. I am therefore justified in saying that the spectra of carbonate and the products of its dissociation are identical with those of sulphate and the products of its dissociation. To recapitulate, these spectra have nothing in common with the spectra of sodium, potassium, lithium, calcium, or strontium.

(To be continued).

ON THE INVERSION OF SUGAR BY SALTS.*

By J. H. LONG.

(Concluded from p. 162).

Zinc Sulphate.

A SOLUTION containing 50 grms. of sugar and 10 grms. of the sulphate in 100 c.c. showed, when fresh, a rotation of $32\cdot98^\circ$ for 100 m.m. After heating forty-five minutes in boiling water, the rotation was reduced to $18\cdot42^\circ$ for the same tube.

Potassium Aluminum Sulphate.

With a solution containing 50 grms. of sugar and 5 grms. of the alum in 100 c.c. a rotation of 33° was found immediately. A portion was heated one hour in the water-bath to 100° , and on cooling to 20° was polarised again, showing now a rotation of $-9\cdot99$. The heated solution became slightly cloudy, but the original remained clear through the several weeks it was kept.

Lead Nitrate.

A fresh solution with 50 grms. of sugar and 10 grms. of the salt in 100 c.c. showed a rotation of $33\cdot13^\circ$. A portion, heated one hour to 100° , showed, after cooling to 20° , a rotation of $-9\cdot65^\circ$ in the same tube.

Lead Chloride.

Some chloride was made by precipitation of the nitrate by sodium chloride. The product was re-crystallised from hot water, and washed repeatedly on a filter with cold water. About 2 grms. of the moist precipitate was mixed with 50 grms. of sugar in water enough to make 90 c.c., and heated until it dissolved. On cooling, the volume was made to 100 c.c. A part of the chloride separated. The rotation was now found to be $23\cdot52^\circ$. The mixture was shaken, and a portion transferred to a flask with capillary stopper, where it was heated one hour to 100° . After cooling, the rotation was found to be $-7\cdot53^\circ$.

Cadmium Chloride.

A fresh solution with 50 grms. of sugar and 8 grms. of the chloride in 100 c.c. gave a rotation of $32\cdot91^\circ$. After heating to 100° it was reduced to $-9\cdot50^\circ$.

Mercuric Chloride.

The original solution of 50 grms. of sugar and 5 grms. of chloride in 100 c.c. gave a rotation of $33\cdot22^\circ$. A portion was heated an hour to 100° and became turbid, depositing on cooling a fine white precipitate. The clear liquid showed a rotation of $-10\cdot80^\circ$. A second portion was heated a shorter time, to the beginning of turbidity only. It was quickly cooled and polarised, showing a rotation of $-4\cdot82^\circ$. By prolonged heating more of the precipitate is formed. It appears to consist of mercurous chloride only.

The salts tested above, while commonly called neutral, are those in which the base is very weak when compared with the acid. It is such salts that show in solution an acid reaction with certain indicators, and the parallelism between the phenomena observed here and that of the inversion of sugar by acids naturally suggested itself. The following further test with a solution of ferrous iodide was therefore made:—This solution contained, in 100 c.c., 50 grms. of sugar and 10 grms. of the iodide. It polarised when fresh $32\cdot41^\circ$ in the 100 m.m. tube. A number of small phials were nearly filled with this solution, and they were heated in a thermostat through different times, as shown below. The phials were made of selected glass, not readily attacked, and before use were heated some hours with hydrochloric acid. They were then washed and boiled with distilled water, and dried. Before being placed in the thermostat they were closed with rubber stoppers having a capillary tube through the per-

* From the *Journal of the American Chemical Society*, vol. xviii., No. 2, February, 1896

foration. The upper end of this extended above the water in the thermostat. The capillary opening was sufficiently fine to prevent any appreciable evaporation of the syrup while being heated. The water in the thermostat was kept at about 77.5° . Phials were removed from time to time and cooled quickly, so that the contents could be examined in the polarimeter. The following results were found:—

Time of heating in minutes.	Observed rotation.
0	32.41°
30	28.00°
60	26.25°
90	26.15°
210	24.61°
390	18.48°
570	16.60°
810	4.70°

These figures show a rapid, but an irregular, change in the rotation with the time, but as the temperature was not maintained with great accuracy, and as some of the phials were more exposed to the light than others, greater uniformity could not be expected.

To determine whether or not the inversion proceeds according to the law of Wilhelmy, a second series of experiments was made, in which the temperature was carefully regulated, and in which the small phials holding the sugar solutions were wrapped in tin-foil for protection against the light. The temperature in the last series of experiments was too low to permit them to be completed in a reasonable time. It was therefore brought to 37.5 for the following tests:—

The amounts of sugar and ferrous iodide were the same as before, but greater care was taken in the preparation of the solution. Several samples of high grade commercial sugar were tested, and one was selected which satisfied all requirements as to purity. For 250 c.c. of solution 125 grms. of this sugar are dissolved in a small quantity of water in a graduated flask by aid of heat. Then 20.5 grms. of the pure iodine, sublimed with potassium iodide, are weighed out and mixed in a flask with 50 c.c. of water and 7 grms. of pure fine iron wire. The action of the iodine on the iron begins soon, and must be checked after a time by dipping the flask in cold water. Finally, when the action is practically complete, as shown by the disappearance of the iodine and change of colour to greenish brown, the solution is boiled to make the reduction to the ferrous condition perfect. The amount of iron taken is largely in excess of that which can combine with the iodine. The ferrous solution is now allowed to cool to 50° to 60° C., and filtered into the cooled sugar solution made as above. The last traces of iodide from the flask and paper are washed down into the syrup by aid of a little boiled and cooled water. Finally, the whole volume is made up to 250 c.c. by the addition of distilled water. In this manner a solution is secured which contains, in 100 c.c., 50 grms. of saccharose and 10 grms. of ferrous iodide, and which is practically free from inversion. The specific rotation of the strong pure syrup is 66.5° ; that prepared with the iodide is 64.82° , as found from the mean of many closely agreeing determinations. It will be noted that this lower specific rotation is about the same as that found for the solutions of the other salts described above. The decrease in the rotation is apparently not a result of inversion.

The method of preparation of the syrup of ferrous iodide as described in the Pharmacopœia leaves a product slightly inverted, because of the higher temperature of mixing the sugar and iodide solutions. When portions of the syrup made as just described are heated in boiling water an hour, in flasks with capillary stoppers to prevent evaporation, the rotation is reduced to -11.5° at 20° for the 100 m.m. tube. This value is almost identical with that calculated from the experiments of Gubbe (*Ber. d. Chem. Ges.*, 1885, 2207), viz., -11.31° for the rotation produced

by the inversion of 50 grms. of cane-sugar in 100 c.c. The presence of the excess of iodide seems to be without much influence on the specific rotation of the invert sugar.

In the experiments given below, the rotations were found in a 100 m.m. tube at 20° . The reading before heating was 32.41° , and this is taken as the initial rotation instead of the theoretical 33.25° . Applying the Wilhelmy-Ostwald formula we have—

$$\text{Nat. log. } \frac{A}{A-x} = Ct,$$

in which A represents the total amount of sugar present and may be measured by the total change in the rotation. It is therefore $32.41^{\circ} - (-11.5) = 43.91^{\circ}$. x represents the amount of sugar inverted at the time, t , and is measured by the decrease in rotation at that time. $A-x$ represents the sugar remaining, and the velocity of the inversion should be proportional to this. The table below gives the results of a series of experiments. The solutions were warmed two minutes before the counting of the times, t , began, as this was found necessary to bring them to the proper temperature. This, of course, introduces a small error into the calculation. The values in the fourth column are obtained by the use of common logarithms.

t min.	Observed rotation.	x	$\log \frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
30	28.50°	3.91°	0.04050	0.00135
60	24.85°	7.56°	0.08206	0.00137
120	17.80°	14.61°	0.17569	0.00146
180	13.35°	19.06°	0.24723	0.00137
240	6.32°	26.09°	0.39165	0.00163
300	4.32°	28.09°	0.44335	0.00148
420	-9.00°	41.41°	1.24461	0.00296

The results of the last column are sufficient to indicate that the inversion follows the general law shown by Wilhelmy to hold for the action of weak acids on sugar solutions. The values of—

$$\frac{1}{t} \log. \frac{A}{A-x}$$

are not constant, but, considering the conditions of the experiment, must be considered close enough until the last one is reached. The solution of the sugar is a very strong one, containing 50 grms. in 120 c.c., and from such a degree of concentration no great regularity can be expected. The variation in the amount of water present, as the saccharose becomes changed into dextrose and levulose, must have some influence on the progress of the reaction, and one of the fundamental conditions of the Wilhelmy experiment is therefore not accurately observed. It has frequently been pointed out that the constant—

$$\frac{1}{t} \log. \frac{A}{A-x}$$

may be quite irregular when calculated from tests on very strong solutions. The values are really constant only when the solvent is so greatly in excess that slight changes in it, in the progress of the reaction, may be neglected. In the present case about 2.1_0 grms. of water disappear in the formation of the new molecules, and this from a solution already very strong. Part of the irregularity in the constant may doubtless be explained in this manner. An accidental exposure to light during the last interval of the heating may partly account for the change in the last value.

It has been found by later experiments, some of which are still in progress, that with dilution of the solutions much more uniform results may be secured, approaching, in fact, those obtained from the action of weak acids alone.

The cause of the inversion of strong sugar solutions by these heavy salts is undoubtedly to be found in their condition of partial hydrolysis by the solvent. The acid ion in each case is a strong one, while the basic ions are all

relatively weak. Indeed, it has been suggested by Walker and Aston that the amount of hydrolysis in solutions of certain salts may be approximately measured by comparing the speed of inversion with that of known amounts of weak acids. The method can be easily applied to a large number of solutions of moderate concentration. Further investigations with special reference to ferrous salts are now in progress.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 11, March 16, 1896.

New Zirconium Carbide.—H. Moissan and M. Lengfeld.—Pure zirconia and carbon if heated in the electric furnace outside of the arc produce a carbide of the composition CZr , well crystalline and not decomposable by water at any temperature from 0° to 100° . This fact is very curious, because zirconium, which in the classification of Mendeleeff approximates to thorium, differs from it in some respects, since its carbide is very stable, whilst thorium carbide decomposes cold water with the formation of acetylene, ethylene, methane, and hydrogen. The colour of this zirconium carbide is grey with a metallic aspect. It is not affected by air, whether dry or moist, even at 100° . It scratches glass and quartz with ease, but it has no action upon ruby. The hydracids attack this carbide readily; hydrofluoric acid in the cold, hydrochloric at 250° , hydrobromic at 300° , and hydriodic at 400° . At a dull redness it burns in oxygen with much lustre. If kept in the liquid state in the electric furnace it dissolves carbon, which, on cooling, it deposits in the state of graphite. Water and ammonia have no action upon this chloride, either at the ordinary temperature or at dull redness. Concentrated nitric acid attacks zirconium carbide with violence. Oxidising agents, such as potassium nitrate, permanganate, and chlorate, attack it with energy; the action of the chlorate is explosive. Potassium has no action at its melting-point, but melted potassa dissolves it with ease.

The University of Glasgow invites the Academy to be represented at the fiftieth anniversary of the professorship of Lord Kelvin.

Principle of an Accumulator of Light.—Charles Henry.—It would be easy at present to devise an arrangement permitting us to store up solar light, and to give it out again in the night at any time desired. But an accumulator of light based upon cold would have no chance of becoming practical except in the polar regions.

Structure and Composition of the Alloys of Copper and Zinc.—Georges Charpy.—(See p. 168).

Part played by Alumina in the Composition of Glass.—Léon Appert.—The introduction of alumina into glasses prevents, or at least retards, denitrification produced by slow and repeated reductions of temperature. The presence of alumina in a glass enables us to substitute without inconvenience, and even with advantage, for a part of the alkaline base its equivalent of lime. The use of alumina may be extended to window-glass and to drinking-glasses. It may be best introduced in the state of felspar.

Journal für Praktische Chemie,
New Series, Vol. li., Part 15.

Researches from the Chemical Institute of the University of Kiel.—These consist of an investigation, by Th. Curtius and A. Blumer, on the action of hydrazin hydrate upon benzoin and desoxybenzoin.

On Dimolecular Nitriles and their Derivatives.—Ernst von Meyer.—This extensive treatise consists of a collection of facts which do not admit of abridgment.

MISCELLANEOUS.

Professor Wyndham R. Dunstan, F.R.S., has been appointed Director of the Scientific Department of the Imperial Institute, which has hitherto been under the temporary direction of Sir Frederick Abel. The principal work of this department is to investigate new or little known products from India and the Colonies, and to advise in reference to their commercial utilisation. Already much valuable work has been accomplished in this direction. With the aid of an increased grant from the Royal Commissioners of the 1851 Exhibition, further additions to the staff of this department will be made, and the laboratory, which was fitted up in 1894, with the assistance of a grant from the Goldsmiths' Company, will be considerably extended.

Royal Institution.—On Tuesday next (April 14th) Professor James Sully will begin a course of three lectures on "Child-study and Education"; on Thursday (April 16) Professor Dewar will begin a course of three lectures on "Recent Chemical Progress"; and on Saturday (April 18) Professor W. B. Richmond, R.A., will begin a course of three lectures on "The Vault of the Sixtine Chapel." The Friday Evening Meetings will be resumed on April 17th, when Professor G. Lippmann will deliver a discourse on "Colour Photography."

MEETINGS FOR THE WEEK.

- MONDAY, 13th.—Society of Arts, 8. (Cantor Lectures). "Precious Stones," by Prof. Henry A. Miers, M.A.
— Society of Chemical Industry, 8. "Estimation of Moisture in Wood Pulp," by R. W. Sindall. "A Study of Comparative Affinities in the case of certain Salts of Ammonia," by Watson Smith, F.I.C. Medical, 8.30.
TUESDAY, 14th.—Royal Institution, 3. "Child-Study and Education," by Prof. James Sully, M.A.
— Institute of Civil Engineers, 8.
— Medical and Chirurgical, 8.30.
— Photographic, 8.
WEDNESDAY, 15th.—Society of Arts, 8. "Early English Organ Writers," by Burnham Horner.
— Meteorological, 7.30.
— Microscopical, 8.
— Geological, 8.
THURSDAY, 16th.—Royal Institution, 3. "Recent Chemical Progress," by Prof. Dewar, F.R.S.
— Institute of Electrical Engineers, 8.
FRIDAY, 17th.—Royal Institution, 9. "Colour Photography," by M. G. Lippmann.
— Quekett Club, 8.
SATURDAY, 18th.—Royal Institution, 3. "The Vault of the Sixtine Chapel," by Prof. W. B. Richmond, R.A.

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THE CHEMICAL NEWS.

Vol. LXXIII., No. 1899.

18 APR 96

POWER OF RESISTANCE OF CERTAIN LIQUIDS AND OF SOME SOLIDS TO THE PASSAGE OF THE RÖNTGEN RAYS.

By M.M. BLEUNARD and LARESSE.

In a paper communicated to the Academy in the sitting of March 2nd we have explained the experimental method to which we have had recourse in undertaking this study; we now give some of the results at which we have arrived.

To express these results we have thought it indispensable to give to them coefficients which we call coefficients of penetration or of translucency; but we hitherto only employ this notation by way of simple indications or points of comparison, reserving to give a photometric method which will permit us to appreciate with precision the power of the resistance to penetration of substances by the Röntgen rays.

Our scale of coefficients increases with the transparency of the liquids, *i.e.*, that in one and the same experiment we give to the liquid which allows itself to be most easily traversed the coefficient 10, whilst complete opacity answers to 0.

We indicate below the results at which we have arrived by multiplying the experiments, and by varying on the sensitive plates the disposition of the liquids, so as to escape every error which may spring either from the intensity or the direction of the Röntgen rays, or from the sensitive plates themselves. The results given have always agreed.

I. Influence of the Degrees of Concentration.—We have exposed to Röntgen rays solutions of alkaline chlorides, bromides, and iodides, of various strengths. Sodium bromide may serve as a type.

Solution of sodium bromide at	5 per cent	Coefficients.
"	"	10
"	"	6
"	"	3
"	"	2

As will be seen, there is no proportionality; it tends rapidly towards a limit, which is the saturation of the liquid.

II. Influence of the Non-metal.—Family of fluorine, chlorine, bromine, and iodine. Solutions of the same concentration.

Results.—Sodium	Coefficients.
fluoride	10
" " chloride	8
" " bromide	6
" " iodide	5

The Röntgen rays have so much the greater difficulty in acting upon the plates through the solutions, as the atomic weights of the non-metals are higher.

III. Influence of the Metal.—Family of lithium, sodium, potassium, and ammonium. Solutions all of the strength of 20 per cent.

Results A.—Lithium	Coefficients.
bromide	10
" Sodium bromide	8
" Potassium bromide	3
" Ammonium bromide	3
B.—Sodium iodide	10
" Potassium iodide	4

The opacity increases therefore with the atomic weight of the metal; ammonium seems to form an exception, as its opacity is sensibly equal to that of potassium.

We have studied the influence of the metal in certain other absolutely different saline solutions.

Water coefficient	Coefficients.
A.—Sodium sulphate	10
Copper sulphate	9
B.—Sodium nitrate	5
Potassium nitrate	8
Uranium nitrate	7
C.—Zinc chloride	1
Iron chloride	4
Manganese chloride	5

As in the case of the alkaline metals, the opacity of these different solutions has always increased with the atomic weight of the metal. Uranium nitrate, in particular, opposes a great resistance to the passage of the rays.

IV. Study of certain Solids.—The results obtained are still very incomplete. We intend pursuing these studies, still we are already able to give the following results:—

Family of carbon, silicon, and boron: carbon is transparent, and communicates its property to organic compounds; graphite and lamp-black are transparent for the Röntgen rays. It is the same with naphthalene, anthracene, and all the following bodies:—Gelatin, camphor, picric acid, fluoresceine, celluloid, fatty matters, alcohol, petroleum glycerin. Silicon is transparent, and seems to communicate its transparency to amorphous silica and asbestos. Boron is moderately transparent.

Family of sulphur, selenium, tellurium: opaque, with the exception of sulphur, which is slightly transmissive.

Family of phosphorus and arsenic: opaque.

The results of our experiments on the greater or less resistance to the X rays, of the different solids which we have submitted to experiment agree exactly with the results obtained by Maurice Meslans, which formed the subject of a memoir submitted to the Academy on February 10th, 1896.

In fine, the opacity of substances seems to increase with the atomic weights (for saline solutions) of the metal and the non-metal.

Application.—One of us, M. Bleunard, has had the idea of applying the opacity of the alkaline bromides to the photography of characters written with an ink containing potassium bromide. A letter written with such ink, and placed in an envelope, has been completely and legibly reproduced on the sensitive plate.

We intend continuing these researches, extending them also to gases, researches which hitherto have been merely sketched.—*Comptes Rendus*, cxxii., p. 723.

ON A MEANS OF COMMUNICATING TO THE RÖNTGEN RAYS THE PROPERTY OF BEING DEFLECTED BY MAGNETS.

By A. LEFAY.

HAVING undertaken some researches on the Röntgen rays, I thought it might be useful so examine if there was not produced a change in their nature parallel to the phenomenon of the discharge of electrified bodies induced by these rays. Considerations founded on certain analogies have led me to suppose that if such a fact is exact, the modified rays ought to be sensitive to the action of a magnetic field. Under this idea I undertook, on March 4th, the following experiment:—

Below a Crookes tube, and at about $\frac{1}{2}$ c.m. from the most brilliant part, I placed a screen of lead perforated by an aperture of 2 m.m. in width; at 0.04 metre lower, a second screen of lead, having a slit of 5 m.m. in width, completely closed by a leaf of silver excessively thin, supported by a platinum wire of 1.5 m.m. in diameter,

placed exactly in the axis of the opening and opposite the silver leaf.

As it is seen, this arrangement allows us to project upon a sensitive plate placed below the shadow of a platinum wire, by the aid of a sheaf of rays determined by the two slits.

In order to modify these rays I connect the leaf of silver to the negative pole of the induction-coil, which actuates the tube so that the sheaf which traverses it has necessarily undergone the action of electrification.

The electrified rays pass then between the armatures of an electro-magnet capable of producing a field of about 400 C.G.S. units, the lines of force of which are parallel to the slits; they then meet the sensitive plate, duly surrounded with black paper, and fixed on an invariable support.

In order to show the existence of a deviation, even if very feeble, I place, during the first half of the experiment, on the right part of the sensitive plate, a screen of lead, which I cause to slide over the left part at the moment when the direction of the current in the electro-magnet changes. In this manner the reciprocal distance of the two segments of the shadow thrown by the wire gives the measure of the double deviation produced by the magnetic field.

In a first experiment, placing the sensitive plate at only 8 c.m. from the armatures of the electro-magnet, I obtained a proof on which I could observe a deviation almost imperceptible, and up to a certain point capable of being attributed to an optical illusion.

It is no longer the same if we carry the plate to the distance of 15 c.m.; we then obtain a proof like that which we have the honour of submitting to the Academy, and which leaves no doubt as to the exactitude of my hypothesis.

As to the direction of the deviation, it is determined by the same rule as that of the magnetic deviations of the cathodic rays in the interior of the Crookes tube.

I repeated the same experiment, under exactly the same conditions, *without electrifying the second screen*, and I obtained two shadows which prolong themselves exactly, which is conformable to the fact already known—that an electric fluid is without sensible action on the Röntgen rays.

Not having yet at my disposal other sources of electricity than the coil itself, which serves for the working of my tube, it has not been possible for me to repeat my experiments on electrifying the silver leaf by methods different from that indicated in this paper. This is a gap which I hope soon to fill up. — *Comptes Rendus*, cxxii., p. 713.

THE MECHANICAL ACTION EMANATING FROM CROOKES TUBES.

By J. R. RYDBERG.

IN No. 6 (Feb. 10, 1896) of the *Comptes Rendus*, MM. Gossart and Chevallier have shown that, in the neighbourhood of a Crookes tube, a radiometer set in motion by an extraneous heat adjusts itself before the tube with a fixed orientation after some pendulum oscillations.

The results of these offer an especial interest, because they seem to indicate an exact method of measuring the intensity of radiations if we can demonstrate that the mechanical actions observed have the same origin as the photographic action.

I have therefore repeated the experiments cited, and have obtained the same results. But on employing an ordinary electric pendulum to see if it was possible to produce these phenomena in air at the ordinary pressure, I have ascertained that all the actions observed with the radiometer derive their origin from the well-known stratum of positive electricity with which the external anti-

kathodic surface of the Crookes tube is covered during the discharges. The adjustment of the radiometer, the pendular oscillations around a position of equilibrium, the influence of the distance of the tube on the force exerted, show themselves as absolutely identical with the actions which we observed on approximating to the radiometer a conductor charged positively and of the same form as that of the tube.

As to the permeability for mechanical action, the bodies mentioned as transparent are dielectrics, whilst the opaque bodies are good conductors, which, not being insulated from the earth, have hindered the influence of the electric stratum of the tube upon the metallic wings of the radiometer.

On enclosing the radiometer in a Faraday's cylinder, formed of a thin leaf of tin, which does not arrest the photographic action, it is found that the radiation of the tube produces no more mechanical action than does—under the same conditions—a conductor charged with electricity. Under such circumstances I have been able to obtain Röntgen's photograph through a radiometer, without perceiving the least trace of mechanical action.

The persistence of the adjustment of the radiometer after the current has been interrupted, evidently derives its origin from the same source, the electric charge of the glass being lost only slowly in the ambient air. On removing in any manner the external charge of the tube, we find that the action upon the radiometer disappears instantly if the influence has not lasted long enough to induce electric strata on the sides of the radiometer.

All the modifications which, according to authors, the field of mechanical force undergoes by magnets, by electric currents, &c., are explained equally by variations of the electric fluid on the introduction of conductive bodies. A magnet only acts in this manner, no difference being perceptible between the actions of the two poles.

From all these facts we conclude that the phenomena observed by MM. Gossart and Chevallier are due to the influence of the external surface of the tube on the metallic wings of the radiometer, and have nothing to do with the Röntgen rays. — *Comptes Rendus*, cxxii., p. 715.

AN IMPROVED METHOD OF ANTHRACENE ASSAYING.

By HENRY BASSETT.

SINCE the publication of my "Note on Anthracene Testing" (*CHEMICAL NEWS*, vol. lxxi., p. 202) much of my spare time has been devoted to working out the new method therein referred to. My original object in undertaking these experiments was to find out some reliable method of discriminating between the commercial A and B qualities; as any conclusion based on the appearance of the quinones in the first stage of the usual process is (except in extreme cases) of very little value, or actually misleading, for several reasons, such as difference of percentage, and especially from differences in the character of the other hydrocarbons in the sample, and, consequently, of the products formed by their oxidation. These causes are not only sufficient to modify the appearance of the crude quinones, but also to alter their weights, as I have ascertained by experiments with pure anthraquinone, with and without the addition of known quantities of hydrocarbons and by-products.

The improved test which I now bring forward depends on the action of nitric acid, under special conditions, on the crude product of the oxidation by chromic acid. The earlier experiments in this direction were made by oxidising in the usual way, and then adding a certain quantity of nitric acid to the contents of the flask, and continuing the boiling an hour longer. Next day the dilution with water, washing with alkali, and treatment with fuming sulphuric acid were carried out as usual.

A large number of experiments made in this way gave results which, though promising, were found to be unsatisfactory in some respects, owing to the complications arising from the presence of the oxidation products in the solution, and for other reasons which would take too long to discuss in the limits of this paper.

I will now describe the method finally adopted, which has given most satisfactory results in every respect in an extended series of experiments with samples of widely different character.

The oxidation is carried out precisely in the usual manner (using 15 grms. chromic acid of about 98 per cent and free from sulphuric acid). Next morning dilute with 400 c.c. water, allow to stand for three hours, filter, and wash with cold water only; then dry the quinone on the filter in the water-oven.

Then open the filter, detach the quinone, and introduce it into a flask of the usual size, by means of a funnel with a short and wide neck, and a glass rod, using a small wash-bottle containing the conventional quantity of 45 c.c. glacial acetic acid to rinse the filter-paper, rod, and funnel. The operation is easily effected with absolutely no loss. Then add 2.5 c.c. of the chromic acid solution (= 1.5 gm. chromic acid) and 10 c.c. ordinary pure nitric acid of sp. gr. 1.42, and boil one hour with condensing tube.

Next morning dilute with 400 c.c. water, allow to stand three hours, filter, wash first with water, then with boiling 1 per cent alkali, and finally with hot water as usual. The quinone is then washed into a flat dish, dried at 100°, mixed with ten times its weight of pure concentrated sulphuric acid (not the fuming acid), and heated for ten minutes on the water-bath. It is then left all night, to absorb moisture, in a tray of water covered by a glass plate, diluted, filtered, and washed with water, boiling alkali, and hot water, exactly as in the ordinary way, and finally dried and weighed, &c.

There are several points worth noting as to the above; the first being that the presence of a small quantity of chromic acid is essential. Experiments with nitric acid alone always showed the presence of small quantities of impurities which rendered the filtration slow and unsatisfactory, and the final product retained the usual brownish colour. Only a small part of this chromic acid is reduced, although the solution becomes green. A second important point is that no difference in the results is caused by slight variations in the quantity of nitric acid used, or in the time of boiling. Of this I have satisfied myself by repeated experiments.

The effect of the treatment is indicated by the reduction in the weight of the first product as compared with a companion experiment by the ordinary test, and also in a striking manner by the colour produced on the addition of fuming sulphuric acid, which is a more or less dark brown with the ordinary test (except in the case of pure or nearly pure anthracene), while by the new method it is a clear orange colour, becoming lighter on heating—in fact, the quinone is so far purified by the preliminary treatment that the use of fuming sulphuric acid is absolutely unnecessary, as I have proved to my own complete satisfaction by a large number of comparative experiments giving identical final weights in both cases; the only difference being that the product when using the ordinary concentrated sulphuric acid is better crystallised. Lastly, with the ordinary test the colour of the final product, especially with B qualities, is more or less brownish; but with the new test it is with all samples, good or bad, a beautiful clean yellow colour, and on sublimation shows very much less carbonisation.

I must not omit to mention that a very careful examination of the final product, both by ignition with sodium and subsequent treatment with iron salts, &c., and also by heating with solution of sulphide of sodium (an exceedingly delicate test) has shown it to be perfectly free from nitro-compounds.

The following table gives the results obtained with

a fairly representative number of commercial and other samples of anthracene:—

	Ordinary test.	New test.	Loss in units.	Percent. loss on value by ord. test.
1. Commercial sample B	34.92	33.26	1.66	4.7
2. " B	32.78	31.20	1.58	4.8
3. " A	19.60	19.35	0.25	1.3
4. " A	51.19	50.68	0.51	1.0
5. " B	39.29	38.65	0.64	1.6
6. Residual product ..	18.28	16.31	1.97	10.8
7. " ..	9.24	7.06	2.18	23.6
8. Regained anthracene .	12.41	11.60	0.81	6.5
9. Experimental product	43.74	42.50	1.24	2.8
10. Commercial sample A	13.87	13.57	0.30	2.2
11. " B	35.82	34.63	1.19	3.3
12. " A	32.23	31.84	0.39	1.2
13. "Pure" anthracene..	95.27	95.02	0.25	0.26
14. Washed sample . ..	61.76	61.72	0.04	0.06
15. " ..	81.75	81.15	0.60	0.73
16. Commercial sample A	82.00	81.75	0.25	0.30
17. " B	36.38	35.78	0.60	1.6
18. " B	31.37	30.52	0.85	2.7
19. " A	32.31	31.42	0.89	2.7
20. " A	41.64	40.83	0.81	1.9

The letters A and B opposite the commercial samples in the above list represent the quality usually ascribed to them in the trade. It will be seen that two of the A samples, Nos. 10 and 19, show a loss of *over* 2 per cent on the value by the ordinary test; and that two of the B samples, Nos. 5 and 17, show a loss of *under* 2 per cent. I am inclined to think that these are instances where a comparison of the results obtained by the two methods may lead to a reliable conclusion as to the quality; and also that this particular percentage loss might fairly be taken as a sort of boundary line.

The new method necessarily takes a day longer than the usual test; but I venture to think that experience will prove it to have distinct advantages in the valuation of commercial anthracenes; and I may point out, in conclusion, that it is also well adapted for the testing of crude anthraquinones.

36A, St. Andrew's Hill, E.C.

ON THE PRODUCTION OF STEEL FOR STEEL CASTINGS IN SMALL BESSEMER CONVERTERS.

By SERGIUS KERN, M.E., St. Petersburg.

NOWADAYS several systems of working small Bessemer converters have been introduced; for instance, Robert, Walrand, Tropinas.

In the CHEMICAL NEWS (vol. lxxiii., p. 111) we gave a short description of the Walrand system as worked at the Franco-Russian Works, St. Petersburg.

As several difficulties may arise elsewhere, we think it needful to make the following remarks:—

1. In calculating the charges, it is preferable to have a final product (castings) of the following average composition:—

Carbon.. ..	0.25—0.30 per cent
Silicon	0.25 "
Manganese ..	0.75 "

The joint percentage of phosphorus and sulphur must not exceed 0.08 per cent. In my process I prefer also to have in the steel 0.10 to 0.15 per cent of chromium, which is introduced with the initial charges in the form of chrome-ironstone, mixed with a $\frac{1}{4}$ per cent of lime. Such a mixture is placed with the charges made for the cupola, in the case of small Bessemer process, or, with the

charges prepared for the crucibles, in the crucible-steel process. The chief constituent of the latter charges is soft Siemens-Martin steel (scrap) of clean composition (for instance, boiler-plate scrap, coming from hole punching). My process of chromium crucible cast steel was proposed in 1878 (*Proceedings of the Iron and Steel Institute*, 1878, vol. i., p. 231). Now I find that the addition of clean raw chrome-ironstone ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) in the form of small pieces, in the quantity of one pound to every eighty pounds of the charge, makes a great improvement in the tenacity of steel castings.

2. All steel castings to be annealed in furnaces; small dimensions in layers of charcoal, and, better, in furnaces used for copper crucible melting. In such furnaces, an iron plate is placed on the fire-bars; next is placed a layer, 6 inches thick, of charcoal, then about 5 cwts. of small steel castings, which are covered with a layer of charcoal 6 inches thick. The lid of the furnace is closed, and the seams are lined with clay. After thirty hours the articles are drawn out, and the operation repeated a second time.

3. We recommend the use for the bottom of the converters good fire-bricks of pyramidal sections, about 10 to 12 inches high; one brick for each tuyere. The lining of the sides is made of a neutral material; lump of chrome-ironstone cemented with a mixture of powdered mineral with lime (3 parts to one part).

4. After the over-blow, the slag is drawn out by means of iron bars inserted into the converter, and fluid silico-spiegel is added (about 5 per cent, containing 10 per cent of silicon and 20 per cent of manganese). Sometimes it is suitable to add also a $\frac{1}{2}$ per cent of 80 per cent ferro-manganese. All this being added, the metal is quietly mixed by iron bars; the converter remaining all this time in a horizontal position, and *no—even quite short—over-blow is made*. Such over-blows for mixing the additions only spoil the quietness of the metal—what inventors, it seems, do not understand, as they often produce over-blows at this part of the process, which certainly spoil the metal, giving rising steel.

5. In order to avoid the last-mentioned nuisance, the ladles must be red-hot before pouring steel into them, and about 0.1 per cent of aluminium must be thrown into them.

We must conclude our short note by saying again that chrome-ironstone has a marvellous effect on steel, when properly applied. As a paint for steel mouldings, we used for several months Stephen's silica moulders' paint, and with good effect, too.

INCREASE IN TEMPERATURE OF CELLULOSE ON ABSORPTION OF ATMOSPHERIC MOISTURE.

By CLAYTON BEADLE and O. W. DAHL.

ONE of us observed that anhydrous cellulose rose in temperature whilst taking up moisture from the atmosphere, and that this rise of temperature appeared to have some relation to the increase in weight (*Nature*, xlix., 457; and *CHEMICAL NEWS*, lxxi., 1).

The above experiments were done with cotton-wool alone. We have carefully repeated these experiments, but using, in addition to cotton-wool (whose fibres were 20–30 m.m. in length), cotton mechanically disintegrated by a dry process (fibres reduced to 1–1.5 m.m.), and a finely-powdered amorphous form of cellulose, which we shall refer to as "viscoid." Viscoid is obtained by treating cotton with strong alkali and carbon disulphide, dissolving the cellulose thiocarbonate obtained in water, and regenerating the cellulose as a gelatinous mass by heat. The mass is broken up, washed free from by-products, dried down, and ground to powder.

In all cases the moisture was removed from the samples

by placing them in a water-bath. In the case of the cotton-wool the percentage is reckoned, and the weight taken before placing in water-bath. In the cases of the disintegrated cotton and pulverised viscoid, the weight at which the samples remain constant is reckoned at 100, and the other weights calculated on this.

It will be noticed by examining the curves for the cotton-wool (Fig. 1) that the two curves run fairly closely, except in the centres, where they diverge considerably. This difference we are unable to explain. It will be noticed, also, that the final weights are short of the air-dry weights by about 0.75 per cent. This appears to be due to the loss of something other than water when the fibre was heated. The disintegrated cotton, which is chemically identical with the cotton-wool, gains much less before it comes to a constant weight. The curves in this instance are much more regular. The disintegrated cotton resembles the cotton-wool in that it becomes constant in weight in about the same period of time, viz., about one hour.

In the case of the powdered viscoid (Fig. 2), the fine gives the most regular curve, but starts from a higher point than the coarse. These two were tried with a view of seeing whether the coarseness of the grain would affect the curve.

Table I. is a summary of the various determinations of the increase in weight. The weighings were in each case done in a weighing tube, and the material removed from the tube and spread out on a tray for exposure.

The three sets of curves in Figs. 1 and 2 resemble each other somewhat closely, and we are inclined to think that the physical condition or structure of the cellulose does not materially affect the character of the curve.

One thing is apparent from these experiments, and that is that the percentage of moisture taken up decreases with the fineness of the cellulose. This is true with cellulose in the fibrous form, such as cotton, as well as with viscoids. The fact that large masses of viscoid have a much higher hygroscopic moisture than viscoid after pulverising lends support to this view. It is also noticeable that, *ceteris paribus*, the curve becomes more uniform with the fineness of the particles of the cellulose. Thus, we notice that the cotton-wool curves are somewhat irregular, but that the same after disintegration are more regular. The coarse powdered viscoid is also much less regular than the fine powdered.

In order to determine the rise in temperature, the cellulose in each, after drying in the water-bath and allowing to cool to the temperature of the atmosphere in a weighing tube, was placed round the bulb of a sensitive thermometer; and a similar thermometer placed at a distance of about four inches was used to indicate the temperature of the atmosphere. The cotton-wool was merely tied on to the bulb of the thermometer, but the pulverised cotton and viscoid were contained in a cage of thin wire gauze, so as to allow free access of the air. The readings are contained in Table II. The curves in Figs. 3 and 4 represent temperature of the cellulose when the temperature of the atmosphere is reduced to a straight line. The two lower curves in Fig. 3 are given by cotton-wool. The lower curve was distorted somewhat by the fact that the temperature of the air did not remain constant. Certain close resemblances between the two curves for cotton-wool can, however, be noticed. The curves for the disintegrated cotton are much more regular and run much closer. Here, again, we see that the fineness tends to regularity. There is, however, an important difference between disintegrated cotton 1 and 2: 1 rises from the beginning, but 2 gives a dip below the atmospheric temperature during the first two seconds. It will be noticed that cotton-wool reaches the temperature of the surrounding air about the time that the weights become constant; whereas the disintegrated cotton is still more than 4° above.

The curves with the powdered viscoid show in each case a rapid fall in temperature during the first minute.

FIG. 1.—Increase in Weight of Dry Cotton by Exposure to the Air. P.c. on air.

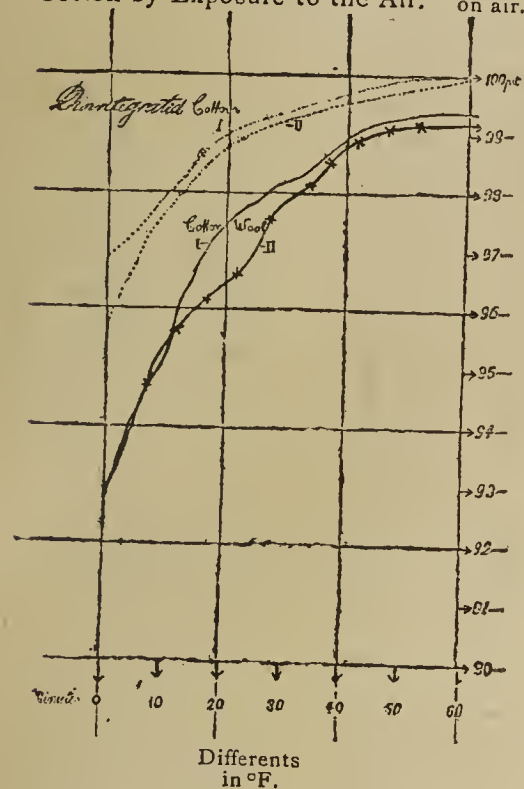


FIG. 2.—Increase in Weight of Dry Viscoid Powdered by Exposure to the Air. P.c. on air-dry viscoid.

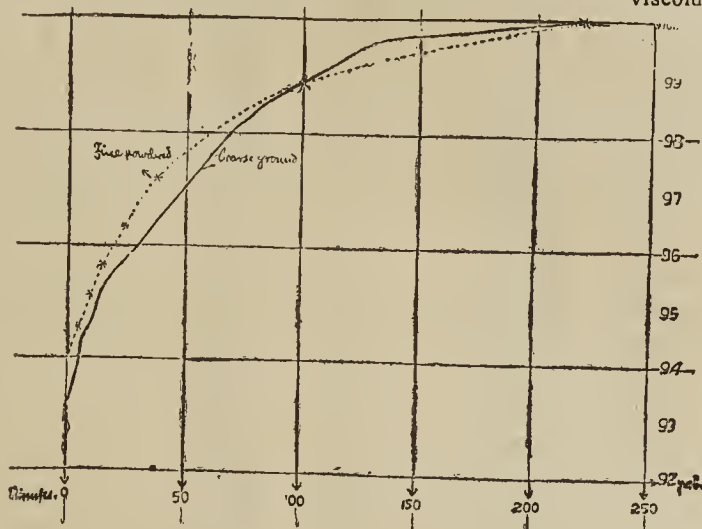
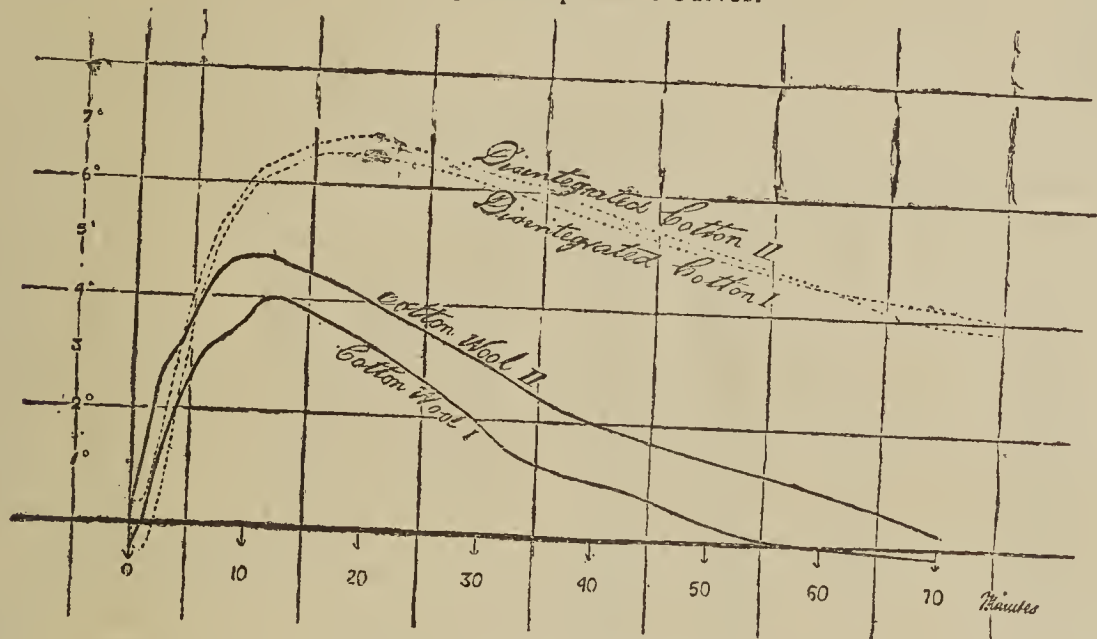


FIG. 3.—Temperature Curves.



Differents in °F.

FIG. 4.—Temperature Curves.

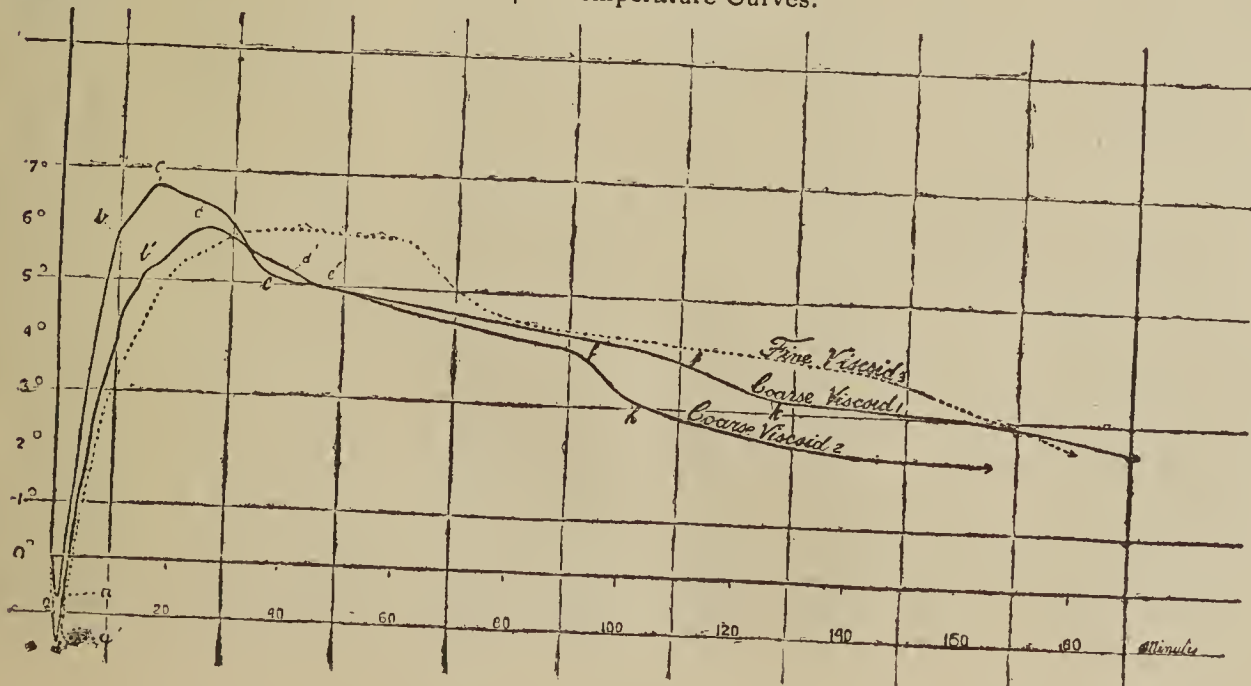


TABLE I.—Increase in Weight by Exposure to the Air of—

COTTON-WOOL.				DISINTEGRATED COTTON.				Viscoid.		Fine Powdered.	
I.		II.*		I.		Coarse Powdered.					
Min.	P.c.	Min.	P.c.	Min.	P.c.	Min.	P.c.	Min.	P.c.	Min.	P.c.
0	92'7	0	92'85	0	96'9	0	93'2	0	94'0		
1	93'1	1	93'10	2	97'1	1	93'3	5	94'55		
2	93'5	2	93'3	4	97'27	2	93'4	10	95'1		
3	93'7	3	93'7	7	97'61	3	93'65	15	95'65		
4	94'05	4	93'9	10	98'0	4	93'75	25	96'35		
5	94'25	5	94'2	13	98'27	5	93'90	37	97'2		
6	94'5	6	94'55	16	98'65	6	94'25	100	98'9		
7	94'75	7	94'75	20	99'0	7	94'40	220	100		
8	94'9	8	95'00	30	99'35	8	94'45	230	100		
9	95'05	10	95'35	40	99'70	9	94'5				
10	95'25	12	95'65	50	99'95	10	94'6				
12	96'05	17	96'20	60	100'00	11	94'75				
13	96'30	22	96'60			12	94'85				
14	96'40	27	97'55			13	95'0				
15	96'7	32	98'15			14	95'15				
18	97'25	37	98'55			15	95'20				
20	97'45	42	98'90	0	95'77	20	95'55				
22	97'70	47	99'05	7	97'26	30	96'00				
24	97'80	52	99'15	17	98'52	40	96'50				
25	97'90	62	99'15	23	98'97	50	97'05				
29	98'15			35	99'40	70	98'05				
31	98'20			45	99'65	80	98'35				
36	98'60			60	99'95	90	98'65				
41	99'00			75	100'00	100	98'90				
46	99'20					115	99'25				
51	99'30					145	99'70				
55	99'35					200	99'95				
60	99'35					220	100'00				

* For this series see CHEM. NEWS, vol. lxxi., p. 1.

TABLE II.—Temperature.

DISINTEGRATED COTTON (exp. to the Air).					
I.			II.		
Min.	Air.	Cell.	Min.	Air.	Cell.
0	63.8	63.8	0	53.9	54.2
1	64.0	63.4	1	53.9	54.2
2	64.1	64.1	2	54.0	55.0
3	64.1	65.1	3½	54.0	56.5
4	64.3	66.6	5	53.9	57.9
5	64.3	67.8	6	53.9	58.5
6	64.4	68.6	8	53.9	59.4
7	64.5	69.4	10	53.9	60.0
8	64.7	70.0	12	54.0	60.4
9	64.9	70.5	14	54.0	60.6
10	65.0	70.9	18	54.0	60.8
11	65.0	71.1	20	54.0	60.9
13	65.1	71.4	25	54.0	60.6
15	65.4	71.9	30	53.9	60.2
20	65.6	72.1	35	53.9	60.0
30	66.0	72.1	40	53.8	59.5
40	66.5	72.0	45	53.6	59.0
60	66.5	71.0	50	53.9	59.0
120	64.0	66.0	60	54.1	58.6
180	66.6	66.7	75	54.2	58.0
			90	54.0	57.0
			105	54.0	56.5

COTTON-WOOL (Exposure to the Air).

I.			II.		
Min.	Air.	Cell.	Min.	Air.	Cell.
0	55.6	55.1° F.	0	61.8	62.0
1	56.0	56.0	1	62.4	63.4
2	56.1	56.9	2	62.6	64.8
3	56.2	57.7	3	62.7	65.5
4	56.3	58.4	4	62.9	66.0
5	56.4	59.0	5	63.0	66.6
6	56.5	59.5	6	63.0	67.0
7	56.7	59.9	7	63.0	67.4
8	56.8	60.1	8	63.2	67.8
9	56.9	60.4	9	63.3	68.0
10	57.0	60.7	10	63.4	68.1
11	57.0	61.0	11	63.5	68.2
12	57.0	61.0	12	63.6	68.3

COTTON-WOOL (Exposure to the Air). (Continued).

I.			II.		
Min.	Air.	Cell.	Min.	Air.	Cell.
13	57.1	61.1	13	63.8	68.4
18	57.5	61.0	15	63.9	68.4
23	58.0	60.9	20	63.8	67.9
28	58.2	60.4	25	63.8	67.4
33	58.9	60.3	30	63.7	66.7
38	59.0	60.0	35	63.7	66.1
43	59.2	60.0	40	63.6	65.6
48	59.6	60.0	45	63.5	65.1
53	89.9	60.0	50	63.4	64.8
58	60.0	60.0	60	63.4	64.3
70	60.6	60.4	70	63.4	63.7

VISCOID (Exposure to the Air).

I.			II.			III.		
Min.	Air.	Cell.	Min.	Air.	Cell.	Min.	Air.	Cell.
0	61.8	61.0	0	62.0	62.0	0	63.8	63.6
1	62.0	60.5	1	62.0	61.3	1	64.0	62.3
2	62.0	61.0	2	62.0	62.0	2	64.0	63.1
3	62.0	62.0	3	62.0	62.7	3	64.1	63.8
4	62.0	62.8	4	62.0	63.9	4	64.1	64.3
5	62.1	63.6	5	62.1	65.0	5	64.2	65.0
6	62.2	64.2	6	62.1	65.6	6	64.2	65.5
7	62.3	65.0	8	62.1	66.9	7	64.3	66.1
8	62.4	65.5	10	62.0	67.8	8	64.4	66.8
9	62.5	66.0	12	62.0	68.1	10	64.7	67.8
10	62.5	66.5	15	62.0	68.6	12	64.8	68.5
11	62.5	66.9	17	62.0	68.7	13	64.9	68.8
12	62.5	67.1	20	62.0	68.7	15	64.9	69.2
13	62.6	67.4	21	62.0	68.6	20	64.9	70.1
14	62.7	67.7	22	62.0	68.5	30	65.2	71.0
15	62.8	68.0	25	62.0	68.4	40	65.0	71.0
17	62.9	68.15	30	62.0	68.1	60	64.0	69.8
20	63.0	68.6	35	68.0	62.7	70	64.0	69.0
25	63.0	69.0	40	62.9	68.0	80	64.5	68.9
35	63.5	69.0	50	62.7	67.6	140	62.9	66.7
45	64.0	69.0	60	62.6	67.4	180	65.0	67.5
100	62.7	66.8	90	62.4	66.4	260	67.1	69.0
160	63.0	66.0	100	63.9	67.1	300	65.0	66.9
280	62.5	63.8	130	64.0	66.4	330	65.7	67.5
340	62.5	63.8	160	64.0	66.2	360	66.0	67.4

We are entirely at a loss to account for this fall. The temperature then suddenly rises. A glance at the two curves given with the coarse viscid shows that they resemble one another very closely. Thus, the points *a, b, c, d, e, &c.*, correspond with the points *a', b', c', d', e', &c.* With the finely-ground viscid we find, again, that the curve is much more regular, and in addition to this, we see that when the maximum is reached, the temperature remains almost stationary for about fifteen minutes; whereas with the coarse viscid the temperature falls immediately after reaching the maximum. With the exception of this, the curves for the coarse and fine viscid in a large measure resemble each other. It is impossible at present to draw any conclusion from these curves as to the nature of these changes, and we must await the issue of further work for an explanation.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 173).

The Electric Spectra of Barium.—On several occasions I have instituted researches on the electric spectrum of chloride and oxide of barium, obtained by the dissociation of chloride or carbonate of barium. These researches have enabled me to enunciate the following facts:—

The colour and luminosity of a spark half a c.m. in length, made by reducing a five c.m. spark, flashing between pure platinum balls coated with fused chloride of barium, barely differed from the colour and luminosity of the same spark in pure air; whilst the same chloride, when moist, coloured the spark a slightly yellowish green. The green colour was more pronounced, with a uniform distance between the balls, when the length of the un-reduced spark was greater. The discharge from a coil with a condenser, giving sparks 15 c.m. in length, between platinum balls coated with fused chloride of barium, was very bright, and coloured greenish yellow.

The colour and luminosity of a spark charged with chloride of barium are therefore functions at the same time of the volatility of the compound and of the intensity of the electrical phenomena.

These facts are more noticeable with oxide of barium. The eye can detect no difference between the colour and luminosity of a 5 c.m. spark and those of a 15 c.m. spark under the same conditions.

On moistening the balls with a saturated solution of oxide, a very pale green colour is seen.

On the other hand, a discharge between the balls coated with the same oxide and half a c.m. apart, from a coil with a Leyden jar capable of giving 15 c.m. sparks, is coloured a strong yellowish green. The luminosity of the discharge is further increased by wetting the balls, coated with fused oxide, with an aqueous solution of the same compound.

Therefore chloride and oxide are similar in this respect, the intensity of the light they impart to a spark is a function of their relative volatility, and of the electrical power employed.

Spectrum analysis of a spark or discharge saturated with chloride or oxide confirms the above facts.

I completely covered the pure platinum balls with chloride, by plunging them several times into this compound when heated fully up to the point of igneous fusion. Without allowing them time to absorb moisture from the air, I arranged them, from 3 to 5 m.m. apart, in front of the slit of the Steinheil spectrocope. Having passed a spark by means of a coil giving 5 c.m. sparks, I detected the barium spectrum, consisting of its characteristic lines, strong at their ends and weak towards their middle, and very faintly coloured, as though the spectrum

of the ends of the spark only was seen. On removing the diaphragm, so as to expose the full height of the field of the spectrum, I became certain that from one-half to two-thirds of the length of the lines was missing, according to the distance between the coated balls.

I repeated these observations very often, and there can be no doubt as to their accuracy.

Having noted the result, without interrupting the sparks, I wetted the coated balls with a saturated solution of chloride, by means of a small platinum spoon attached to a glass tube. The spark was immediately coloured green, and, without exception, all the lines became perfect, and at the same time acquired their proper colour and luminosity.

I tried to repeat this when using the large Hilger instead of the Steinheil spectrocope. When using successively three and five Iceland spar prisms, I failed to notice the lines faded away either in their middles or at their ends; all of the few I could see were complete, but extremely faint.

I moistened the coated balls by means of a chloride solution, and immediately the luminosity of the barium spectrum increased to the same degree as that of the spark, and I saw a perfect electric spectrum of barium.

I replaced the chloride by oxide of barium newly prepared by the action of an oxyhydrogen blowpipe on chloride. When using the Steinheil spectrocope I found the same facts in a more marked degree. *The lines were still more incomplete, more evanescent towards the centre, and the colour of the parts seen was also less bright.* To perfect the lines, it was sufficient to increase the luminosity of the spark. This result was attained by wetting the dry oxide with an aqueous solution of itself, or even with pure water; but it is not possible to reproduce in this manner the colour intensity of the lines in the spectrum of dry chloride, which is more volatile than dry oxide.

These facts agree with those noted by M. Fiévez, and the explanation he gives appears to me to be incontestable. It is well known that he attributes the existence or absence of imperfect lines to the degree of luminosity.

The luminosity of the electric radiations from baryta is comparatively slight. For instance, when examining an electric barium spectrum formed by analysis of a spark from 2 to 5 m.m. long, passing between platinum balls coated with dry chloride or oxide of barium, or even wetted with a saturated solution of either of these salts, if a Bunsen burner charged with thallium, or one of its compounds, be placed behind the spark charged with baryta, so that thallium rays pass through this latter, the barium spectrum is seen to be extinguished and replaced by the thallium spectrum. By interposing a movable screen in front of the thallium flame and behind the balls coated with the baryta compound, I could, at will, cause the appearance or disappearance of the electric spectrum of barium, or the flame spectrum of thallium, using either the Steinheil, Duboscq, or large Hilger spectrocope, the latter fitted with three Iceland spar prisms.

The rays emitted by the Bunsen flame charged with metallic thallium were so intense that I succeeded in completely extinguishing the barium spectrum in an electric discharge from an induction-coil capable of giving 15 c.m. sparks, but reduced to 5 m.m.

It remained to find out whether radiations from a flame or electric arc charged with thallium were capable of interfering with an arc spectrum of baryta.

Regarding the electric spectrum of barium, my repeated observations of its compounds made under varying conditions confirm Bunsen's statements about the spectrum of its chloride. I found the spectrum of oxide to be identical with that of the chloride, as regards the colour intensity of corresponding lines and the complete absence of the sodium line. I found that the spectra of an electric spark, discharge, and arc, made by means of a battery of thirty very large Bunsen cells, were formed entirely of the same extremely sharp lines. This fact is very remark-

able, and it is not observed to the same degree with the electric spectra of compounds of calcium and strontium, notwithstanding their brilliancy.

I took very great care in enumerating and determining the positions of the lines in the electric barium spectrum, by means of the Steinheil spectroscope, and in comparing my results with Bunsen's determinations, made by means of a spectroscope of the same pattern.—

		I found Div.	Bunsen gave Div.
In the red ..	Two strong lines at	36.50	35.50
		44.00	43.50
	Two weak lines „	44.50 45.80	43.80 45.50
In the yellow	A strong line „	51.00	51.00
	A weak line „	52.00	52.00
In the green	A strong line „	60.40	61.00
	A weak line „	63.00	65.00
In the bluish green ..	A strong line „	82.00	86.00
	A weak line „	83.00	87.75
In the blue	A strong line „	101.75	108.50

These results agree when an allowance is made, by calculation, for the difference in the refractive power of the prisms of the two spectroscopes used.

The flame and electric spectra of barium show both common and specific lines. The bands in the flame spectrum from 35.0 to 37.0, from 43.5 to 46.0, and from 54.5 to 66.25, on the Steinheil spectroscope, corresponding to from 34.0 to 36.0, from 43.0 to 46.0, and from 61.0 to 63.0 on the Bunsen spectroscope, are represented by strong or weak lines in the electric spectrum at 36.5, 44.0, 44.5, 45.8, and 60.4 on the Steinheil spectroscope, corresponding to 35.5, 43.5, 44.0, 45.5, and 65.0 on the Bunsen spectroscope. The strong bands from 39.0 to 41.0, the bands from 54.5 to 55.25, from 56.0 to 57.0, from 63.5 to 66.0, at 67.75, at 70.75, from 72.5 to 80.0, and finally the nebulous line from 84.25 to 86.0, on the Steinheil spectroscope, corresponding to from 55.0 to 56.0, from 57.0 to 58.0, from 65.5 to 68.0, from 70.0 to 74.0, and from 89.0 to 91.0, on the Bunsen spectroscope, are not found in the electric spectrum.

The strong lines in the electric spectrum seen with the Steinheil spectroscope at 51, 82, and 101.7, corresponding to 51, 86, and 108.5 on the Bunsen spectroscope, are entirely wanting in the flame spectra. I enumerated the bands in the flame spectrum, made in oxyhydrogen gas, and also determined the position of the lines in each of the spectra, by superposing the two types as accurately as possible. These differences, which have been the subject of most minute investigation on my part, were first detected by Bunsen, and shown by him in the plates accompanying his work; I consider them to be absolutely demonstrated.

The difference between these two types of spectra is so great that, even after having produced and reproduced them from the same body, one is hardly convinced that they belong to an element: I was likewise struck with astonishment when I first compared, by a most accurate superposition, the electric with the flame spectra of the same chloride of barium, and using the same instrument.

The electric spectrum has been shown to be unchangeable; in the colour intensity of corresponding lines, the spectrum of the weakest spark saturated with dry chloride of barium is identical with the spectrum of the most powerful electric discharge or arc I have at my disposal. Every attempt I made, by raising the temperature, to change either of the flame spectra into the electric spectrum, ABSOLUTELY failed, and *vice versa*. Judging from my own experience, I must consider that the flame and electric spectra of barium are not convertible the one into the other.

Barium, then, in this respect resembles calcium, strontium, sodium, and lithium; the flame and electric spectra of these metals are, in fact, of different types, however much each may appear to resemble the other.

The difference noticed between the flame spectra is probably due to inequality of temperature,—at least experience tends to that conclusion. Can the difference between the complete flame spectrum and the electric spectrum be due to the same cause,—that is to say, to the inequality of the temperatures of an oxyhydrogen blowpipe and an electric spark, causing radiations of different intensities? As a matter of fact, this relative intensity can cause to appear or prevent the appearance, or at least the *visibility*, of certain lines.

(To be continued).

THE COMPOSITION OF WATER. A SHORT BIBLIOGRAPHY.

By T. C. WARRINGTON, B.A.

(Concluded from p. 171).

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"On the Occlusion of Hydrogen by Copper."
J. C. S., (1879), xxxv., p. 232.
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"On the Variability of the Law of Definite Proportions."
Bull. Soc. Chim., (1883), [2], xxxix., pp. 257 and 263.
Amer. Journ. Sci., (1883), [3], xxvi., p. 63.
In the course of the paper (Expt. 6) the author finds that the ratio O : H, on burning hydrogen with copper oxide, is not constant with varying conditions.
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"Das Verhalten des Wasserstoffs zu Blei und anderen Metallen."

Sitzungs. Akad. Wien., (1891), c., C, II. b, p. 618.

Monat. für Chem., (1891), xii., p. 642.

Ber., (1892), xxv., Ref. p. 187.

The amount of hydrogen occluded in various metals, including copper, is found.

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"Atomgewicht des Wasserstoffs."

Lehrbuch der Allg. Chem., (1891), 2nd Ed., i. p. 43.

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"The Atomic Weight of Oxygen."

Nature, (1892), xlv., p. 151.

Chem. News, (1892), lxxv., p. 311.

The author notices a rise in the determined values of the atomic weight of oxygen, and regards this as due to an actual rise in atomic weight.

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"Détermination des Poids Atomiques par la Méthode Limite."

Compt. Rend., (1893), cxvi., p. 753.

The observations of Dumas on the Composition of water are used as an example.

(67). 1893. G. HINRICHS.

"Détermination du Poids Atomique Véritable de l'Hydrogène." (Note).

Compt. Rend., (1893), cxvii., p. 665.

Chem. News, (1893), lxxviii., p. 269.

The observations of several observers are reduced by the limit method (65).

Of subordinate points, the *purity of the hydrogen* used is discussed in Nos. 5, 12, 13, 18, 20, 25, 28, 30, 34, 37, 38, 39, 44, 46, 49, 50, 61;

The *purity of the oxygen* used in Nos. 5, 12, 13, 18, 20, 23, 25, 28, 30;

The *occlusion of gases by copper* in Nos. 34, 39, 43, 48, 49, 54, 63;

The *purity of copper and copper oxide* used in Nos. 35, 38, 39, 44, 47, 48, 49, 50;

The *reduction of weighings to vacuo* in Nos. 34, 35, 36, 37, 38, 39.

Criticisms of previous work will be found in Nos. 5, 9, 14, 15, 17, 18, 20, 21, 22, 25, 26, 30, 36, 37, 38, 39, 42, 44, 48, 50, 53, 56, 57, 58, 59, 60, 61, 62, 64, 65, 66, 67.

The Sixty-eighth Meeting of German Naturalists and Physicians.—This Congress will be held this year from September 21st to 26th at Frankfort-on-the-Main. The President of the Chemical Section (No. 3) is Dr. Theodor Petersen, and the Secretary Dr. Martin Freund. It is requested that papers to be read and demonstrations to be submitted may be announced to these gentlemen up to the end of May. It will be remembered that the German term "Naturforscher," which we are obliged to translate by "Naturalist," includes all persons who study any department of natural science.

NOTICES OF BOOKS.

The Medical Register. Printed and Published under the Direction of the General Council of Medical Education and Registration of the United Kingdom pursuant to an Act passed in the Year XXI. and XXII. Victoria, Cap. XC., entitled "An Act to Regulate the Qualifications of Practitioners in Medicine and Surgery." 1896. London: Printed for the General Medical Council at Her Majesty's Printing Office, and Published and Sold for the Council by Spottiswoode and Co., 54, Gracechurch Street, E.C.

By far the greater part of this goodly volume is taken up with a catalogue of the registered practitioners in the United Kingdom, or if not resident in such kingdom, qualified to carry on their profession therein if such be their pleasure.

There are abstracts of the original Medical Act of 1858, with its amendments, technically so-called. There are laid down the rights and privileges of registered practitioners, and the disabilities of unqualified pretenders acting as physicians or surgeons. It is to be remarked that these disabilities are not so stringent as to prevent the wholesale exercise of quackery, and that under their sway the charlatan is often able to amass wealth such as the most eminent physician cannot reach. The difficulties in the way of striking out unqualified persons from the register are often serious. An important desideratum is the formation of an Imperial register for the entire dominions of Her Majesty. We may note with satisfaction as a far-off step in this direction the compilation of an Imperial Pharmacopœia.

The Dentists' Register. Printed and Published under the Direction of the General Council of Medical Education and Registration of the United Kingdom, pursuant to an Act passed in the Year XLI. and XLII. Victoria, Cap. XXXIII. entitled "An Act to Amend the Law relating to Dental Practitioners." 1896. London: Printed for the General Medical Council at Her Majesty's Printing Office, and Published and Sold for the Council by Spottiswoode and Co., 54, Gracechurch Street, E.C.

We have here the "Dentists' Act" in full. Among the provisions here recognised as binding there are some whose necessity, or their *raison d'être*, is not very clearly apparent. Thus no medical authority is to impose upon candidates for examination an obligation to adopt, or refrain from adopting, the practice of any particular theory of dentistry or dental surgery! Surely a case so unlikely need scarcely have been specially provided against. It would appear that a very large proportion of the dentists here registered were in practice before July 22nd, 1878.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 12, March 23, 1896.

Invisible Radiations emitted by the Salts of Uranium.—Henri Becquerel.—Already inserted.

Observations on M. Becquerel's Communication.—L. Troost.

Observations on a Paper by Charles Henry entitled "On the Principle of a Luminous Accumulator."—Henri Becquerel.—The author shows that the prevention of the emission of light by intense cold had been studied by Canton as far back as 1764, as well as by Becquerel, sen., and by Raoul Pictet.

Application of the X Rays for the Diagnosis of Surgical Affections.—M. Lannelongue.—Instances of the successful application of the Röntgen rays in the detection of surgical injuries.

Researches on Rare Earths contained in Monazitic Sands.—P. Schützenberger and O. Boudouard.—This paper will be inserted in full.

Quantities of Nitric Acid contained in the Waters of the Seine and its Principal Affluents.—Th. Schlösing.—The essential conclusion of the present paper is that the rivers in the entire basin of the Seine have similar phases as regards nitric acid. They present simultaneously their highest standards after a prolonged depression of the temperature has suspended the aquatic vegetation and suppressed the influx of drainage water. Consequently, it is possible to select the time and the place for taking samples of water for ascertaining its maximum standard of nitric acid.

On a Means of Imparting to Röntgen Rays the Property of being Deflected by a Magnet.—(See p. 177).

Mechanical Action emanating from Crookes Tubes.—J. R. Rydberg.—(See p. 178).

Origin of the Röntgen Rays.—Jean Perrin.—The author finds that Röntgen rays are developed at points where the cathodic rays are arrested by any substance whatever, and do not appear to develop at other parts. These rays diverge in all directions; only certain substances, such as crystals, absorb them rapidly.

Researches concerning the Properties of the X Rays.—Prince B. Galitzine and A. de Karnojitzky.—This paper will be inserted in full.

Reduction of the Time of Exposure for Röntgen Photographs.—Georges Meslin.

Procedure allowing an Abridgment of the Time of Exposure for Photography with the X Rays.—M. Basilewski.

Reduction of the Time of Exposure in Photography with the X Rays.—A. Imbert and H. Bertin-Sans.—These three papers will be summarised jointly.

On the X Rays.—M. Piltschikoff.—On employing a Puluj tube excited by a Wimshurst machine I have obtained a photographic proof in two seconds. This duration of exposure was amply sufficient, the phosphorescent plate of the tube being at the distance of 4 c.m. from the sensitive plate. The author has demonstrated the non-influence of electrostatic actions upon the X rays. He has also shown, along with other physicists, the transparency of the diamond for these rays, and their discharging action upon an electrolysed body (sodium amalgam).

Power of Resistance of certain Liquids and Solids to the Passage of the Röntgen Rays.—MM. Bleunard and Labesse.—(See p. 177).

Action of the X Rays upon Precious Stones.—Abel Buguet and Albert Gascard.—The transparency of aluminium for the X rays led us to think that its compounds might retain some of this property. Crystallised alumina, which, next to diamond, constitutes—under the names of corundum, ruby, sapphire, emerald, topaz, and cat's-eye—the majority of the most valuable stones, distinguishes the latter and its imitations from the above-mentioned stones. Turquoise (aluminium phosphate) is also thus certainly distinguished from its imitations. Natural aluminium mellite (mellite) is almost as transparent as carbon. Fine pearls of small size are less opaque than false ones of the same size, and may be clearly distinguished by the X rays. For large pearls the distinction is not certain.

Three cases of the Surgical Application of Röntgen Photographs.—Pierre Delbet.—This memoir is of great surgical interest, but does not reveal any new properties of the X rays.

The Rays of Röntgen in the Eye.—Dr. Wuilloment.—From experiments on a rabbit, the author concludes that the opacity of the eye to the X rays is not absolute. In a second series of experiments made on a human head the results were negative, notwithstanding very intense radiation and prolonged exposure.

Novel Element contained in Rare Earths bordering on those of Samarium.—Eug. Demarçay.—Already inserted.

Action of Reducing Agents upon the Compounds of Nitroso-ruthenium.—L. Baizard.—The preparation of a ruthenium nitroso-oxide by the action of ammonia upon potassium ruthenate approximates to the preparation of potassium osmiumate by the action of ammonia upon the osmiate.

Amalgams of Molybdenum, and some Properties of Metallic Molybdenum.—J. Ferée.—The properties of molybdenum obtained from its amalgam by distillation *in vacuo* at a low temperature are quite different from those of molybdenum as hitherto obtained. The substance is pyrophoric, ignites in the air, yielding molybdic oxides, which are partially volatilised by the heat liberated. It loses this property if heated above 400°. It becomes incandescent in a current of sulphurous acid, which is entirely absorbed, forming molybdenum sulphide and molybdic oxides. Nitrogen, carbonic acid, and hydrogen sulphide seem to have no action at the ordinary temperature or at a gentle heat. Carbon monoxide is rapidly decomposed.

Products of the Distillation of Wood. (Experiments made on an Industrial Scale).—Ernest Barillot.—The author gives his results in the form of tables.

Isomerism in the Aromatic Series.—Oechsner de Coninck.—The author has already shown that the aromatic isomers resemble each other two by two if submitted to various physical and chemical reactions. The same conclusion is reached on comparing the ebullition and fusion points of the principle aromatic derivatives.

Rhodinol and its Transformation into Menthone.—Ph. Barbier and L. Bouveault.—Not suitable for useful abstraction.

— — —
Journal für Praktische Chemie,
New Series, Vol. li., Part 15.

A Reply by F. Stolz to the Memoir of R. von Rothenburg.—The subject of the discussion is the constitution of the *n*-phenylpyrazolones. The spirit in which it is now conducted may, perhaps, be judged from the opening sentence of the paper now before us:—"In the memoir referred to, R. von Rothenburg advances no new evidence in support of his position, but merely repeats errors which have long ago been refuted, to which he appends a new one of similar value."

On Reductions by means of Phenylhydrazin.—R. Walther.—The author shows that at an elevated temperature phenylhydrazin reacts violently with azobenzene, the products being from the azobenzene, hydrazobenzene, and from phenylhydrazinbenzene with an escape of nitrogen. The author has examined further reductive actions of phenylhydrazin.

Flashing-point of Petroleum.—The *Chemiker Zeitung* of March 28th contains a most thorough-going paper on the petroleum question from the pen of Dr. O. A. Lobry de Bruyn. He pleads for an international agreement on the flashing-point of mineral oils, which should not fall below a minimum of 40° C. Referring to the recognised fact that one death weekly is traced in London alone to lamp accidents, and in the whole of Britain *one daily*, he asks whether a moral question of such gravity should be buried under a heap of dollars?

MEETINGS FOR THE WEEK.

- MONDAY, 20th.—Society of Arts, 8. (Cantor Lectures). "Precious Stones," by Prof. Henry A. Miers, M.A.
- TUESDAY, 21st.—Royal Institution, 3. "Child-Study and Education," by Prof. James Sully, M.A.
- Institute of Civil Engineers, 8.
- Pathological, 8.30.
- Photographic, 8.
- WEDNESDAY, 22nd.—Society of Arts, 8. "The Perfected Photo-chromosome and its Colour Photographs," by F. E. Ives.
- THURSDAY, 23rd.—Royal, 4.30.
- Chemical, 8. "Temperature of Certain Flames," by W. N. Hartley, F.R.S. "Halogen Additive Products of Substituted Thiosinamines," by Augustus E. Dixon, M.D. "Constitution of Cereal Celluloses," by C. F. Cross, E. J. Bevan, and Claud Smith. "Apparatus for the Detection of Boric Acid," by W. M. Doherty. "Ethereal Salts of Optically Active Malic and Lactic Acids," by Prof. Purdie, F.R.S., and S. Williamson, Ph.D.
- Royal Institution, 3. "Recent Chemical Progress," by Prof. Dewar, F.R.S.
- FRIDAY, 24th.—Royal Institution, 9. "The Circulation of Organic Matter," by Prof. G. V. Poore, M.D.
- Physical, 5. "Symbolism in Thermodynamics," by R. A. Lehfeldt. "Adjustment of the Kelvin Bridge," by R. Appleyard. "The Effect of Wave-form on the Alternate Current Arc," by J. Frith.
- SATURDAY, 25th.—Royal Institution, 3. "The Vault of the Sixtine Chapel," by Prof. W. B. Richmond, R.A.

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THE CHEMICAL NEWS.



USE OF NON-UNIFORM MAGNETIC FIELDS IN
PHOTOGRAPHY WITH THE X RAYS.

By GEORGES MESLIN.

I HAD recently the honour of submitting to the Academy the principle of a method destined to abridge the duration of exposure in photography by the X rays. We have seen that it is possible not merely to displace the active fluorescent spot, but to condense it so as to increase its brightness. This condensation is obtained by concentrating the cathodic rays which give rise to it, and this concentration is due to the fact that the field employed is not uniform. It is therefore necessary that the field should present a suitable variation to obtain the desired deformation.

On studying the influence of the variation of the field, both as regards its intensity and its form, we find that:—

1. On operating, *e.g.*, with a horizontal tube and throwing back the cathodic rays towards the upper part of the terminal caps, there is a concentration in the middle vertical plane if the field is decreasing upwards, and an expansion if the field is increasing downwards; there is no variation in dimension if the field is uniform. It is necessary if we employ this arrangement to place the poles below the axis to obtain a suitable variation of the field.

2. We find also that on acting upon the rays in the neighbourhood, so as to throw them back upon the upper horizontal portion of the tube, it is important (to obtain a contraction in the other direction) to employ those parts where the lines of force turn their concavity upwards; the field then fulfils the duty of a cylindrical mirror, and we have a luminous horizontal line in the vertical median plane. We may then condense it in the other direction by increasing the mean intensity of the field.

By utilising these considerations, I have obtained in five seconds a photograph of the bones of the hand of an adult. It was possible to recognise on this proof the traces of a fracture of old date.—*Comptes Rendus*, cxxii., p. 776.

ON THE RAYS OF RÖNTGEN ELECTRISED.

By A. LEFAY.

IN a recent memoir which I have had the honour of submitting to the Academy, I gave a description of an experiment which has enabled me to show the deflection by the magnet of the Röntgen rays modified by a previous passage through an electrified lamella. I now propose to indicate some complementary results relative to these modified rays, which, as an abridgment, I propose calling "Röntgen's electrised rays."

If, instead of electrising these rays by putting in communication the metallic lamella with the negative pole of the induction coil, as I have indicated in the experiment above described, we take as the source the negative pole of a static machine, we observe a deflection in the same direction as that which I have already spoken of. It is no longer the same if we electrise the lamella positively with the same machine; the direction of the deviation is then inverted.

I had in the first place obtained this last result by taking as a source of electricity the positive pole of the Ruhmkorff coil which actuates my Crookes tube; but it

appeared so strange to me, that before announcing it I wished to verify the fact that it is equally produced on employing a source of static electricity.

There exist, therefore, Röntgen's rays electrised both positively and negatively.

The research into the laws which connect the magnitude of the deviation to the intensity of the magnetic field, to the state of electrification of the lamella, and to the nature of the dielectric will form the subject of a more extensive investigation. For the present I must confine myself to the foregoing qualitative indications, pointing out that there must exist between the Röntgen rays electrised negatively and propagating themselves in rarefied air and the cathodic rays the greatest analogy, *perhaps even absolute identity*.

It is convenient, in order to retain the direction of the deviations, to employ the very suggestive procedure devised by Hittorf with reference to the cathodic rays. Let us assimilate the Röntgen flux to a sheaf of conductive wires, indefinite, flexible, and without weight. When they traverse a plate positively electrised, they permit its discharge, and are the seat of an electric movement which flows towards the points with the lowest potentials. When the lamella is electrised positively, the direction of the movement is inverse. In both cases these conductors twist under the action of the magnetic field, and the direction of the deviation is given by Ampère's rule.

I conclude this paper by indicating a fact of a quite different order, though not without interest. It has been remarked that in certain Crookes tubes the degree of the vacuum increases gradually, and that such tubes before long cease acting. This accident happened to my tube about a month ago. I then had the idea of placing it for some time in a stove at 200°, which restored its original properties. Since that time I have continued to make use of it, re-heating it when it began to show signs of weakness. This practical observation perfectly corroborates the recent communication by M. Goury relating to the occlusion of gases by the glass of the Crookes tubes.—*Comptes Rendus*, cxxii., p. 809.

ON THE
DIFFERENT PROPERTIES OF THE INVISIBLE
RADIATIONS EMITTED BY URANIUM SALTS,
AND THE
RADIATION OF THE ANTIKATHODIC
WALL OF A CROOKES TUBE.

By HENRI BECQUEREL.

THE study of the properties of the radiations emitted by the salts of uranium, on which I have already discoursed to the Academy in the foregoing sessions, and to which have to be added some new properties described below, renders it possible to establish important differences between the effects of these radiations and the effects produced by the radiation of the antikathodic wall of a Crookes tube, such as Prof. Röntgen has described and applied.

1. *Double Refraction. Polarisation and Dichroism through a Tourmaline.*

With the purpose of examining if the radiations emitted by the salts of uranium are polarised, I arranged the following experiment:—A slender slice of tourmaline, cut parallel to the axis, and of 0.50 m.m. in thickness, was cut in two; the two halves were juxtaposed so that their axes were rectangular, and the whole was covered by a single plate, parallel to the axis, of 0.88 m.m. in thickness, and the axis of which was parallel to the axis of one of the two halves of the original tourmaline. In these conditions ordinary light is transmitted through the two

tourmalines (the axes of which are parallel), and is arrested through the other half of the system. This total, thus arranged, was placed on a photographic plate, previously wrapped in black paper, and was covered with a lamina of the double uranyl and potassium sulphate. The photographic plate, developed after the lapse of sixty hours, showed very distinctly the silhouette of the tourmalines, and the action through the parallel tourmalines was notably stronger than that through the crossed tourmalines.

This experiment shows therefore at once, for the invisible rays emitted by uranium salts, the double refraction, the polarisation of the two rays, and their unequal absorption through the tourmaline.

The same experiment, repeated with the same tourmalines and the radiation emanating from a Crookes tube, gave a negative result; the two flat layers have absorbed the radiation equally. This result, which has already been signalled by Prof. Röntgen, is in agreement with the absence of appreciable radiation. It does not prove the radiation is not polarised, but merely that the absorption is the same for parallel tourmalines as for crossed tourmalines.

2. Unequal Absorption for different Substances.

The absorption of the two radiations which occupy us, when they traverse the same substances, presents very different characters. We may demonstrate this either by the photographic method, which gives qualitative results, or by the electroscope, which furnishes the relative measurements.

a. Photographic Method.—If we project the radiation of a Crookes tube upon a photographic plate wrapped in black paper, and covered with different substances in thin slices, or with small flat tubes filled with different liquids, we observe at first that on a short exposure most substances—except paraffin, which is very transparent, and aluminium, which is a little less so—behave as having opacities very close together. Still we find that water is much more opaque than paraffin, and a solution of uranium nitrate is more opaque than solutions of copper nitrate and gold chloride.

If we expose for a longer time we find that a plate of copper of 0.04 m.m. is traversed, but at a thickness of 0.95 m.m. copper is very sparingly transmissive. Platinum, of the thickness of 0.08 m.m., appears one of the most opaque of the bodies studied. On the same plates there were also zinc, lead, silver, glass, spar, quartz, rock-salt, &c. Glass of 2.13 m.m. in thickness, quartz perpendicular to its axis (2.05 m.m.), spar (1.93 m.m. and 2.40 m.m.), and rock-salt, appeared as little transparent as copper.

The absorption of rays emitted by a salt of uranium is very different. Aluminium and paraffin are always very transparent, but the metals are much more easily traversed by the radiation of a Crookes tube; copper (0.10 m.m.) is very transparent; platinum (0.08 m.m.) equally, but a little less than copper; silver also transmits these radiations, as does zinc; lead (0.36 m.m.) behaves as opaque.

Quartz (4.66 m.m.) and Iceland spar (4.48 m.m.) are very slightly transparent; sulphur (2.01 m.m.) is more so.

We perceive already that the radiations emitted by the salts of uranium traverse the majority of bodies more easily—especially metals—than does the radiation of a Crookes tube.

b. Electroscopic Method.—The discharge of a substance electrified by the radiations having traversed various screens leads to the same conclusion. I have already shown that quartz absorbs less the radiations of the salts of uranium than the radiation of a Crookes tube.

If we cause a Crookes tube to act upon the gold leaves of an electroscope, a plate of aluminium of 0.10 m.m. in thickness transmits an intense radiation, and the collapse of the gold leaves ensues in a few seconds; if we then interpose a plate of copper of 0.10 m.m. in thickness, the gold leaves cease to approach each other, or at least ap-

proach each other extremely slowly. Platinum intercepts the radiation still more.

It is not the same with the rays emitted by the salts of uranium, which traverse copper and platinum much more easily. I give here certain figures measuring the action through these two metals. The experiment was arranged as follows:—A lamella of the double uranyl-potassium sulphate was placed at about 2 c.m. below the gold leaves of the electroscope. I studied then the loss of the latter when this lamella acted alone, or on interposing successively or simultaneously screens formed of sheets of aluminium, copper, or platinum. The sheet aluminium was 0.10 m.m. in thickness, the sheet copper 0.09 m.m., and the sheet platinum 0.035 m.m. The action was measured by the speed of the collapse of the gold leaves, or by the fraction of a degree by which their angle diminishes per second; we know that this decrease is sensibly proportional to the time. The following numbers express the velocities in seconds of an angle and in seconds of time.

Action of a Plate of the Double Uranyl-Potassium Sulphate on the Gold Leaves of an Electroscope.

Nature of screens.	Date and mean hour of movement.	Velocity of collapse.
Without screen	Mar. 28, 1.45 p.m.	28.18
Aluminium screen (0.10 m.m.)	" 3 "	9.42
Copper do. (0.09 ")	" 3.50 "	11.40
Platinum do. (0.035 ")	" 5 "	9.60
Platinum and aluminium superimposed	" 5.50 "	6.53
Without screen	" 6.20 "	33.60
Aluminium and copper superimposed	" 6.40 "	7.44
No screen (next day)	Mar. 29, 5.40 "	33.00

It is perceived that copper and aluminium have approximately the same absorption for the same thickness, that platinum absorbs rather more, and that the absorption of superposed screens is less than the sum of the effects due to each, as in Melloni's experiments on thermochrosis, and as it has been established by Hurmuzescu and Benoist by antikathodic radiation.

The radiations emitted by the lamella of uranium salt are not homogeneous.

In an experiment made last week I observed that the electroscope discharges itself through a screen of copper of 1.40 m.m. in thickness.

The above figures show also that, a short time after exposure to light, the action of the lamella of the double uranium salt was a little stronger. In five hours there is produced a slight decrease, after which the action remains sensibly constant until the next day.

3. On some Peculiar Properties of the Emission of Radiations by the Salts of Uranium.

I have already pointed out the refractive independence of the invisible radiations of the uranium salts, and the emissions of visible radiations of phosphorescence; in particular the uranous salts which are not phosphorescent emit invisible radiations. I have also indicated that uranium nitrate melted, and, having been allowed to crystallise in the dark, was as active as the crystals of the same salt exposed to the light. I have recently satisfied myself that uranium nitrate, dissolved in water, is still as active, although this solution is not fluorescent. This is a new instance of the mutual independence of these two phenomena of emission.

I have likewise examined if these radiations might communicate a sensible phosphorescence to sulphides which had become inactive, or to various specimens of hexagonal blende which I possess. The result has been negative, at least as far as the immediate effect is concerned. In like manner the action of the radiation of a Crookes tube communicates no activity to hexagonal blende, either during the excitation or afterwards on prolonging the exposure during three days.

I have not observed any appreciable difference between the activity of a lamella of the double uranyl-potassium sulphate exposed to the radiation of a Crookes tube and a lamella not exposed. During the direct influence of this radiation upon a photographic plate, the lamella behaves as if opaque. It has then been placed upon another photographic plate, by the side of a lamella of the same salt, and the two lamellæ have given identical impressions.

I must still cite an experiment which seems in contradiction with the phenomena of reflection and refraction which I have observed.

Between two lamellæ of glass of the same thickness (1.83 m.m. in one experiment and 1.37 m.m. in the other) I heaped up powder of glass obtained by pulverising a piece of the same glass, and the powder slightly heaped up dusted the surface of the glass plates. Under these conditions the band of pulverised glass appeared as if opaque to ordinary light. It is known that the radiation of a Crookes tube traverses it with the same facility as a plate of homogeneous glass: this is one of the fundamental experiments of Prof. Röntgen. In the conditions just indicated, and with the radiations emitted by the salts of uranium, the band of powdered glass behaved as strikingly more transparent than the adjoining glass plates. As the quantity of matter traversed is sensibly less, we cannot deduce any certain conclusion from this contradictory experiment.

4. General Considerations.

It would be premature to draw absolute conclusions from the foregoing experiments. If we regarded only the simple phenomena of absorption, we might render an account of the facts by admitting that the radiations emitted by the uranium salts and the radiation of a Crookes tube behave as having different wave-lengths, but the absence of reflection or refraction well established for the radiation studied by Prof. Röntgen establishes a more profound difference. It seems more probable to think that the phosphorescence of the antikathodic spot is only a phenomenon concomitant of an electric phenomenon of which it is the seat, and that it is this electric phenomenon—a sort of effluve, as it results from the experiments of H. Dufour (*Comptes Rendus*, cxxii., p. 460), which provokes the phosphorescence of the photographic plate, and in consequence the reduction of the silver salts by the phosphorescent radiations excited on the spot. As for the phosphorescence of the glass of the Crookes tubes, it is possibly accompanied by radiations analogous to those emitted by the salts of uranium, but a very long exposure would be needed for their manifestations. — *Comptes Rendus*, cxxii., p. 762.

THE STORAGE CELL OF THE FUTURE: A NON-SULPHATING PHOSPHO-ACCUMULATOR.

By H. N. WARREN, Research Analyst.

In this improved form of cell, the old method of using red-lead or peroxide is entirely dispensed with, each plate being composed of pure spongy lead, obtained by pasting lead grids of special construction with a paste composed of litharge and phosphoric and sulphuric acids; drying the so-prepared plate for several hours at a temperature of about 250° F.; further treatment of the same with acids, and continued drying, until finally a biscuit plate is obtained. The plates are next arranged in pile fashion, with alternate plates of amalgamised zinc interposed between the leads, and insulated from each other by means of small carbon blocks, the pile thus formed being immersed in a solution of dilute vitriol. A somewhat violent reaction at once takes place, a copious evolution of gas is given off from the lead plates, and continues so until perfect reduction terminates the action,

the result being a fine porous lead plate, which, after washing to free it from accompanying zinc salts, is most admirably adapted for the further process of forming, which is brought about by insulating the plates by means of suitable material, and actuating upon them with an electric energy varying in quantity as to the size of the plates to form.

The plates now in communication with the positive electrode will, by this treatment, be noticed to have speedily assumed a brown tint, which rapidly increases until the whole of the spongy lead contained therein is converted into peroxide, while at the same time the negative element will be found, upon close examination, to be possessed of a somewhat lighter tint and closer texture.

The plates, having been now perfectly formed, are next rendered non sulphating, by soaking the same in dilute phosphoric acid, or 12 per cent of the same acid may be advantageously introduced into the dilute vitriol bath in the first instance. Plates formed by this treatment will be found to compare most favourably with any others upon the market, being formed in less than half the time, and also, at the same time, being capable of resisting sulphation.

Liverpool Research Laboratory,
18, Albion Street, Everton, Liverpool.

ARSENIC IN COAL.

By W. M. DOHERTY, F.C.S., Government Laboratory, N.S.W.

IN a recent trial in Sydney connected with an arsenical poisoning case, a rather unusual matter was introduced. It was alleged that the person accused of administering the arsenic disposed of the balance in his possession by burning it in a kitchen stove. To ascertain if there was any truth in this allegation, certain samples of soot, flue-dust, ashes, &c, were procured from different parts of the stove, the stove-pipe, and the brick chimney into which the stove-pipe led. These were tested by the Government Analyst for N.S.W., who found in the mixed flue-dust and soot taken from a position in the stove between the fire-place and the pipe that arsenic was present to the extent of 8 grains to the pound of the mixed flue-dust and soot. The soot from the stove-pipe, and also that from the brick chimney, were separately analysed, and traces of arsenic were found in each case. Coal was the fuel used in the stove. It was suggested that the presence of arsenic in soot taken from a place where coal had been burned was not necessarily an indication that arsenic had been added to the fire from some extraneous source, since it is highly probable that arsenic exists naturally in some portions of all coal seams. Therefore, it may have found its way into the kitchen stove in the most innocent manner. It was argued by some scientific men that as it is not uncommon to find strong traces of copper, lead, and other metals, besides occasionally even considerable quantities of sulphide of iron, it is most likely that arsenic may also be present at times in coal. But this argument seemed to lose much of its significance when applied to this particular case; the relatively large proportion of arsenic found in the flue-dust pointed to the conclusion that it did not come naturally from coal, however else it may have come.

There was no available recorded instance of the presence of arsenic in coal; and, so far as I am aware, the question had not yet been touched. In order, then, to discover if it were possible to trace arsenic in New South Wales coals, I obtained various samples of soot taken from flues where coal had been burned for years, and by the kindness of several gentlemen connected with the coal trade, I have been able to test samples from the following mines, which I think fairly represent the coal seams of the colony:—The Vale of Clwydd, Great Southern, South Bulli, Metropolitan, Newcastle-Wallsend, and Greta.

After a series of experiments, and repeated searching analysis, in no instance could I find the slightest trace of arsenic in the samples mentioned.

The work I have been able to contribute to this subject will not, of course, settle the question definitely as to the entire absence of arsenic in all coals; yet it may have a value, inasmuch as it shows that a large number of samples, selected indiscriminately from a number of coal mines, contain absolutely no arsenic.

It should be mentioned that in two instances I found copper and lead; and, in some of the samples, also comparatively large quantities of brasses, which, on separate examination, were found to be arsenic free.

The methods used in the investigation were oxidation with hydrochloric acid and potassium chlorate, and distillation with hydrochloric acid and ferrous chloride. As final tests, the methods of Marsh and Reinsch, and an excellent arrangement of Mayencon and Bergeret's highly sensitive perchloride of mercury test, designed by Mr. W. M. Hamlet, F.I.C., F.C.S., were used in all cases.

As a check on the reliability of the processes, control experiments were made by adding five m.grms. of white arsenic to a weight of coal equal to the quantity operated on (*i.e.*, 100 grms.), and it was repeatedly found to give marked indications of its presence.

ON CEMENTED OPEN-HEARTH OR BESSEMER STEELS.

By SERGIUS KERN, M.E., St. Pete-sburg.

WE cannot certainly venture to say that we were the first to propose the use of open-hearth or Bessemer steels, in the preparation of cemented steel, for the production of special qualities of crucible steel. Anyhow, our short notice on this subject, giving some details of our experiments, appeared in the Russian mining paper *Gorny Listok*, No. 14, 1892.

After successful results in our several times interrupted experiments, we expect to have means for considerable experiments on our process of crucible steel method this coming summer, and we give some few notes on the method which in details is entirely new.

Soft open-hearth steel, containing not more than 0.25 per cent of manganese, phosphorus + sulphur 0.04 per cent, in the form of rolled flat bars ($1\frac{1}{2}'' \times \frac{3}{4}''$), is sheared into bits, $1\frac{1}{2}''$ to $2''$ in length, which are cemented in quantities, by using small cementation furnaces. Where re-heating and puddling furnaces are in constant work, the waste heat of such furnaces may be used in a special way.

The resulting cemented steel containing from 0.85 to 1.15 per cent of carbon, is assorted, and used for the production of special qualities of crucible steel (tools, projectiles, chief parts of ordnance, &c.).

Our process consists in melting such cemented steels, sometimes with a small quantity of wrought iron, and with the additions of certain small quantities of rich silicon iron and chrome ironstone.

The following analysis of a chisel for cold metal working gives an idea of the steel obtained by our process:—

	Per cent.
Carbon	0.95
Manganese	0.30
Phosphorus + sulphur.. ..	0.04
Chromium	0.12
Silicon	0.27

The metal, containing little manganese and impurities, hardens evenly, without cracking. The double-hardening (*double-trempe*) acts beneficially on this steel.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 184).

WITH the object of finding out whether it was possible, by means of pure chloride or oxide of barium, to cause the appearance of one of the characteristic lines of the electric spectrum of calcium or strontium, and especially of the prominent blue lines common to the flame and electric spectra,—in other words, whether barium could be resolved into calcium and strontium, I eagerly profited by the opportunity afforded me by M. Duboscq of making an experiment, on a very large scale, with the electric light plant at Brussels, using either a battery or a dynamo. For this purpose I volatilised, with the help of M. Duboscq, who supervised all the installations, and of M. Romme-laere, some chloride and oxide of barium in the voltaic arc produced in succession by fifty, one hundred, and two hundred very large Bunsen cells, and in the electric arc from a 10,000 c.p. dynamo.

To carry out these experiments, I had to put one end of two pure carbon rods, 10 c.m. long by about 1 c.m. diam., into, and thoroughly coat them with, pure fused chloride or oxide of barium.

These rods were held upright by one end in strong insulated copper clips, 25 c.m. apart, working by means of a rack, with an insulated handle, on a varnished glass stem attached to a thick sheet of plate glass, also varnished. The upper rack was connected to the negative pole, the lower to the positive pole of the battery.

The upper rod, pointed at its free lower end, was adjusted so that its point was exactly in the centre of a cavity in the upper end of the lower rod. This cavity would hold about 1 grm. of fused chloride or oxide of barium.

By means of the insulated racks it was possible, without breaking the insulation, to put the electrodes in contact so as to destroy the arc, or to part them, and so lengthen or vary the diameter of the arc formed by the current already established.

The stem carrying the rods arranged in this manner was placed at a suitable distance in front of the slit of the spectroscope. This distance varied between two and three metres, according to the instrument used.

I adopted the above-described arrangements, because I wished to fix the position of the electrodes, both for examining the electric arc charged with baryta, the electrodes being kept apart, and to examine the light produced by contact of the electrodes in the presence of a barium compound.

Now this condition of absolute steadiness was difficult, if not impossible, to obtain with the regulators I had at my disposal. In fact, in these regulators the electrodes were continually in motion, either approaching till they touched or receding to the limiting length of the arc. It follows from these oscillations that, when using fixed spectroscopes, one is examining a continually varying luminous point; within very small intervals, one sees successively the spectrum of the electrodes in contact, the spectrum of a very short but thick arc, and the spectrum of a long thin arc,—spectra whose constituents are different, but which may be mistaken one for the other on account of the phenomenon of persistence.

Whereas by my arrangement I could, by working the rack, after having established the current (*by putting the electrodes in contact, and heating their ends in an oxygen-hydrogen blowpipe, so as to fuse the chloride or oxide of barium*), adjust the electrodes so as to make the axis of the collimator coincide either with the middle of the arc or with the electrodes in contact.

As regards the barium spectrum, the results were the same. For example, when examining with the Steinheil spectroscope a baryta arc, either short and thick or long

and *thin*, it was impossible to see, for a single moment, in the spectrum, the *blue and violet calcium and strontium lines*.

When using the Duboscq spectroscope fitted with five prisms, and taking *the solar spectrum as a standard*, the eye was not able to perceive in the barium arc spectrum, or in the spectrum of the bright light produced by the contact of the electrodes moistened with the chloride of barium, the blue calcium line, and the blue and violet strontium lines in the position they ought to occupy in the solar spectrum.

On making the slit very narrow, and only allowing a pencil of light about *two or three m.m.* high to pass through it, so as to obtain a spectrum about *1 c.m.* high, bounded by two dark bands, we made the following observations:—

A. Spectrum analysis of an *arc* gave a spectrum which was more strongly illuminated when the arc was short.

Whatever the degree of luminosity, the spectrum consisted of a *continuous* spectrum, on which appeared:—

- 1st. The barium spectrum as it was seen in a spark without a condenser, charged with barium.
- 2nd. The electric arc carbon spectrum, consisting of fine lines more strongly coloured when the arc was short.

B. Spectrum analysis of the bright light formed by the electrodes in *contact*, and entirely surrounded by baryta vapours, showed a very bright spectrum, consisting of a continuous spectrum, on which appeared *only* the electric barium spectrum as it was seen in the arc, side by side with the fine carbon lines.

When the slit is sufficiently narrow, and the distance between the electrodes and the analysers properly adjusted, the electric barium lines can be distinguished so perfectly that it is easy to measure the position of each of them in the spectrum, but excessively fatiguing to the eye on account of the bright illumination of the continuous spectrum.

Following the revision of my spectroscopic researches in collaboration with M. Depaire, I tried to check my research on the arc spectrum of barium. We used a current produced by the Julien accumulators, and also by the Gramme and Siemens dynamos coupled.

The spectroscopes used were:—

- 1st. One with flint-glass prisms made by M. Duboscq, the same as that used by M. Lecoq de Boisbaudran for his work.
- 2nd. One with two half prisms and lenses of quartz, made by M. Hilger.
- 3rd. The new direct-vision instrument designed by Messrs. Liveing and Dewar, also made by M. Hilger.

We used a Gérard regulator to carry the electrodes. The pure carbon rods were *ten c.m.* long by about *one c.m.* diam. The lower end of the upper rod was pointed; the upper end of the lower rod was hollowed to contain about *1 grm.* of fused chloride or oxide of barium.

When looking through the spectroscopes, at a suitable distance in front of the electrodes, we saw *exactly* the same phenomena as those described above, that is to say:—

- 1st. Spectrum analysis of the barium arc, whatever its length or diameter, showed a very bright continuous spectrum, on which was superposed both the electric spectrum of barium, well known through Bunsen's researches, and the fine electric carbon lines such as have been drawn by M. Fievez, without *any trace* of the blue and violet calcium and strontium lines.
- 2nd. Spectrum analysis of the bright light produced by the electrodes *in contact*, surrounded by vaporised barium compounds, showed a continuous spectrum, on which was superposed the electric spectrum of barium only.

Owing to the oscillation of the carbon electrodes in the Gérard regulator, both the above-mentioned spectra were seen alternately, so long as all the chloride or oxide was not volatilised or dispersed too much by the current.

By introducing either chloride or oxide of barium into the arc, by means of a pure carbon spatula of suitable size, and interposing a piece of blue glass between the eye and the arc, so as not to strain the eye, it was possible to see the barium compound melt as soon as it was introduced into the arc, and take a spheroidal form. The spheroid floated in the arc until it was completely volatilised, or, as frequently happened, until it was thrown against the negative electrode, along which it was spread in small drops and scattered to some distance.

By repeating this operation frequently, and analysing the barium arc, whilst it lasted, the stability of the electric barium spectrum under the conditions of the experiment was demonstrated.

It follows from the above that there is no connection between the barium spectra and the spectra of sodium, potassium, lithium, calcium, and strontium.

During the course of the researches I have just described, it has happened that I have met with—either in the flame spectrum or the electric spectrum of a barium compound—*fugitive traces* of the blue lines due to calcium and strontium. When this occurred I was always able to separate, by *chemical methods*, the impurity detected by spectrum analysis. The fact of having been able to effect the separation and of simplifying it, by reducing the flame and electric spectra to constant forms, proves the elementary character of barium.

If this truth had need of further proof, the work I carried out with potassium, lithium, calcium, strontium, and barium furnished me with plenty of evidence.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MARCH 31ST, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, April 10th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from March 2nd to March 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 182 samples examined all were recorded as clear, bright, and well filtered.

We have this month to record an excess of rainfall, after the long period of deficiency since November, 1895; the measured fall at Oxford being 2.45 inches, the 30 years' average 1.50 inches, showing an excess of 0.95 inch.

In spite of this increase of rain, and consequent flooding

of the river, the quality of the water is practically the same as of late, viz., excellent.

Our bacteriological examinations give the following results:—

	Colonies per c.c.
Thames water, unfiltered	2160
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	72
Ditto ditto lowest	16
Ditto ditto .. (12 samples) mean	41
New River water, unfiltered	1938
New River water, from the Company's clear water well	27
River Lea water, unfiltered	1900
River Lea water from the East London Com- pany's clear water well	29

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.

JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 19th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MR. HUGH CANDY was formally admitted a Fellow of the Society.

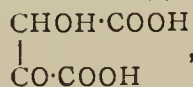
Certificates were read for the first time in favour of Messrs. W. Goodwin, 9, Westminster Gardens, Hillhead, Glasgow; Edgar Hawkins, M.D., Dudley Dispensary; Robert Haslewood Jones, 8, St. Mary's Place, Newcastle-on-Tyne; John McCrae, jun., 264, Calhoun Street, Cincinnati, Ohio; Thomas William Pilley, 33, Grove Hill Road, Denmark Hill, S.E.; Robert Barnabas Pollitt, care of Oscar Guttmann, Esq., 12, Mark Lane, E.C.; Otto Rosenheim, 68, Belsize Park Gardens, N.W.; Walter Dalrymple Severn, 9, Earl's Court Square, S.W.; John Christopher Stead, 42, Grove Green Road, Leytonstone; Edward Channing Wills, Abbey Park, Keynsham, Bristol.

Of the following papers those marked * were read:—

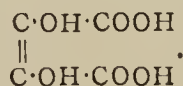
*37. "*The Constitution of a New Organic Acid resulting from the Oxidation of Tartaric Acid.*" By HENRY J. HORSTMAN FENTON, M.A.

This paper gives an account of numerous experiments which the author has recently made with a view of investigating the constitution of the new acid, $C_4H_4O_6$, obtained by the oxidation of tartaric acid in presence of iron, which has been described in former communications.

The molecular weight, basicity, and several characteristic relationships of the acid having been already established, a choice is left between (1) the ketonic formula—



and (2) the dihydroxylic formula—



The acid might assume both forms, or, if represented by the second formula, a fumaroid and maleinoid modification would be expected. The following is a brief summary of the principal results obtained:—

The absence of a ketonic group is demonstrated by the behaviour of phenylhydrazine and of hydroxylamine. These agents have no action whatever upon the methyl and

ethyl esters, and the crystalline compounds which they produce with the free acid are shown to be the respective normal salts.

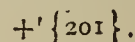
The presence of two alcoholic hydroxyl groups is shown by the actions of acetyl chloride, benzoyl chloride, and acetic anhydride, and the unsaturated nature of the acid is indicated, directly or indirectly, by several of its reactions. These facts leave no doubt that preference must be given to the second formula, and, on account of the great instability of the acid and normal aniline salts, and for other reasons, it is concluded that the acid belongs to the maleic series.

By the action of hydrogen bromide in acetic acid solution, an acid is obtained which has the same composition as the original acid, and many of its properties are similar. But its crystalline form is altogether different, and its acid aniline salt shows a much greater stability in aqueous solution. It is suggested that this product may be the corresponding dihydroxyfumaric acid, the formation of which could be readily understood from two intermediate compounds which have been isolated.

*38. "*The Volume and Optical Relationships of the Potassium, Rubidium, and Cæsium Salts of the Monoclinic Series, $R_2M(SO_4)_2 \cdot 6H_2O$.*" By A. TUTTON, Assoc. R.C.S.

In this communication are presented the results of a detailed investigation of the physical properties of the same 22 salts whose morphological relationships were described in a former memoir (*Trans.*, 1893, lxiii., 337). The main conclusions are as follows:—

1. The whole of the salts of the series exhibit a common cleavage direction parallel to the orthodome—



2. The relative density increases by an approximately constant amount for each of the two specific changes throughout the series, when potassium is replaced by rubidium, or the latter by cæsium; the difference evoked by the former change is larger than that produced by the latter in the proportion of 5 : 4.

3. A similar constant increase occurs in the molecular volume, the replacement of potassium by rubidium being invariably accompanied by an increase of about 9.3 units, while the interchange of cæsium for rubidium results in the larger increase of about 13 units. The determination of the molecular volume is almost exclusively a function of the alkali metal, change of the second metal being practically unaccompanied by any change of volume.

4. The replacement of potassium by rubidium, or the latter by cæsium, is accompanied by a marked increase in the separation of the structural units along each of the axial directions. The elemental distance ratios of any rubidium salt of the series are consequently intermediate between those of the potassium and cæsium salts containing the same second metal. The effect is greatest when cæsium replaces rubidium.

5. The orientation of the variable axes of the optical indicatrix, lying in the symmetry plane, of every rubidium salt of the series, is intermediate between that of the potassium and cæsium salts containing the same second metal. The replacement of rubidium by cæsium is accompanied by a much greater change of orientation than the interchange of rubidium for potassium.

6. The refractive indices of any rubidium salt of the series are without exception intermediate between those of the corresponding potassium and cæsium salts, and nearest to those of the potassium salt. An increase in the atomic weight of the contained alkali metal is accompanied by an increase of refractive power, and the increase in refraction becomes relatively greater as the atomic weight becomes higher.

7. The relative velocities of light vibration along the three axes of the optical ellipsoid of every rubidium salt of the series are intermediate between those along the corresponding directions in the analogous potassium and

cæsium salts. Increase in the atomic weight of the alkali metal is accompanied by an increase of resistance to the vibrations of light waves along each ellipsoidal axis, and this alteration is much the greatest when cæsium replaces rubidium.

8. An increase in the atomic weight of the alkali metal is accompanied by convergence of the values of the velocity along the three axial directions towards unity, and consequently by a diminution in the double refraction. This property is already feeble in the potassium salts, and it is extremely weak in the cæsium salts; the rubidium salts occupy an intermediate position in this respect.

9. Cæsium nickel sulphate differs from the other salts of the series in exhibiting negative double refraction, the usual sign being positive. This fact is directly due to the operation of the preceding rule; owing to the fact that in the potassium nickel salt the two nearest of the three values of the velocity are at their maximum separation for the series, the rule of progressive convergence causes it to happen that in the cæsium salt the third value has approached nearest the intermediate value, and this reverses the sign of double refraction. This interesting fact would have been inexplicable without the rule now established.

10. Another extraordinary result of the rule is afforded in the case of cæsium magnesium sulphate, where, owing to the separation of the two nearest values of the velocity being at its minimum for the potassium salts of the series in potassium magnesium sulphate, the progressive convergence actually results in those two values arriving at unity in the cæsium salt, which consequently exhibits simulated uniaxial refraction phenomena.

11. The whole of the specific and molecular optical constants, calculated by means of the formulæ of either Lorenz or Gladstone and Dale, for every rubidium salt of the series are intermediate between those of the potassium and cæsium salts containing the same second metal. An increase in the atomic weight of the alkali metal is accompanied by a diminution in the specific constants and an increase in the molecular constants, the former being greatest when rubidium replaces potassium, and the latter when cæsium replaces rubidium. These rules are independent of temperature.

12. Excluding the salts containing magnesium, for a reason connected with the statement in paragraph 10, the optic axial angle of every rubidium salt is intermediate between the optic axial angles of the analogous potassium and cæsium salts.

13. In the magnesium salts the progressive change proceeds as usual as far as the rubidium salt, but, owing to the extraordinary relations of the velocities of light vibration when the cæsium salt is reached, as stated in paragraph 10, cæsium magnesium sulphate exhibits specially interesting optic axial angle phenomena. The coincidence of two of the velocity values is only absolute for wave-length 450 in the blue, for which the uniaxial cross and circular rings are produced. Hence the salt exhibits very large dispersion in crossed axial planes for other wave-lengths, and great sensitiveness of the optic axial angle to change of temperature. These remarkable phenomena, almost unique as regards monoclinic symmetry, are the direct result of the rule regarding the velocity of light vibration.

14. A progressive alteration in the optic axial angle occurs upon rise of temperature, the rubidium salts being always affected in an intermediate manner.

15. So completely general are the rules given in the preceding paragraphs, that it is possible to predict the crystallographical characters of the two hitherto unprepared potassium salts of the series containing manganese and cadmium.

16. The final conclusion of the investigation is that the alkali metal R exerts a predominating influence in determining the characters of the crystals of this series, and the whole of the crystallographical properties of the

potassium, rubidium, and cæsium salts containing the same second metal M, are, in the case of every such group throughout the series, functions of the atomic weight of the alkali metal which they contain.

*39. "*Comparison of the Results of the Investigations of the Simple and Double Sulphates containing Potassium, Rubidium, and Cæsium.*" By A. E. TUTTON, Assoc. R.C.S.

The author institutes a comparison of the whole of the experimental results derived from the investigations of the rhombic simple alkaline sulphates and of the monoclinic double salts of the series $R_2M(SO_4)_2 \cdot 6H_2O$. It is shown that the whole of the morphological and physical characters of the crystals of the rhombic normal sulphates of potassium, rubidium, and cæsium, and of any group of the monoclinic double sulphates of the series $R_2M(SO_4)_2 \cdot 6H_2O$, in which those simple salts of the three alkali metals are combined with the sulphates of either magnesium, zinc, iron, manganese, nickel, cobalt, copper, or cadmium, while exhibiting the same symmetry and the general similarities proper to isomorphous series, present well defined differences which are functions, and usually accelerating functions, of the atomic weight of the alkali metal which they contain.

*40. "*The Bearing of the Results of the Investigations of the Simple and Double Sulphates containing Potassium, Rubidium, and Cæsium upon the Nature of the Structural Unit.*" By A. E. TUTTON, Assoc. R.C.S.

The author arrives at the following conclusions:—
(1) The absence of any considerable contraction in volume when the alkaline sulphate enters into the double sulphate, as contrasted with the relatively enormous contraction which occurs when the various atoms combine to form the chemical molecule of the alkaline sulphate, together with the facts that the double salt is only known in the solid crystallised condition, and that many of the individual members of the series are eminently unstable, render it highly improbable that there is chemical union between the molecular constituents of the double sulphates, and indicate that there is no necessity to assume linkage of any kind, but merely aggregation in accordance with such a type of homogeneous structure as ensures that they are always present in the same proportion. (2) In the production of crystals it is not necessary to suppose that any other structural units are concerned than the chemical molecules of the chemical compound in question or of the constituent chemical compounds in the cases of double salts or salts containing water of crystallisation, and the observed fact of the constancy of molecular proportions of the two latter is entirely accounted for by the nature of the type of homogeneous structure in which they find equilibrium. (3) The pedetic or "Brownian" motion of small particles, capillarity, convection currents, or any other slightly agitating forces which assist the chemical molecules to take up this condition of equilibrium necessary for the production of a homogeneous structure, will assist crystallisation. The molecular forces whose domain of action has been shown not to extend beyond a very few molecular distances, need only be concerned in maintaining the general cohesion. (4) Considering the chemical molecule as the structural unit, in general such units will not be endowed with the same symmetry as the crystal; it may have higher, equal, or lower symmetry according to the specific constitution of the molecule. This is in complete accordance with the generalisation of Barlow concerning the homogeneous portioning of space, and the conclusion of Fock derived from the theory of solid solutions. (5) The more heterogeneous the constitution of a crystallised substance, the lower in general is its type of symmetry. (6) The nature of the predominating faces, as being the planes most closely studded with similar "points," together with the directions of cleavage, agree in indicating that the type of homogeneous structure of the simple alkaline sulphates is that of the rectangular pinacoidal

prism, and that of the double sulphates the primary monoclinic prism, probably type 64a of Barlow. (7) The phenomenon of the rotation of the optical ellipsoid of the double sulphates, when the atomic weight of the alkali metal is changed, is completely accounted for by the acceptance of the above simple constitution for the double salts together with the suggestion of Barlow that the orientation of the optical ellipsoid is the resultant of a process of averaging the directional retardations experienced by light waves in traversing the homogeneous structure, due to the arrangement of the molecular matter. The greater amount of rotation when caesium replaces rubidium than when the latter replaces potassium, is thus the direct result of the correspondingly greater increase of volume, largely in a particular direction, which is observed.

*41. "*The Hydriodides of Hydroxylamine.*" By WYNDHAM R. DUNSTAN, F.R.S., and ERNEST GOULDING. The authors have isolated two hydriodides of hydroxylamine, $(\text{NH}_3\text{O})_3\text{HI}$ and $(\text{NH}_3\text{O})_2\text{HI}$, from the interaction of methyl iodide and a solution of hydroxylamine in methyl alcohol, these salts being formed in addition to the trimethylhydroxylamine hydriodide previously described (*Proc. Chem. Soc.*, 1894, 138). The normal hydriodide $(\text{NH}_3\text{O}\cdot\text{HI})$ could not be found. The same hydriodides may be formed by mixing strong aqueous hydriodic acid with the calculated quantity of hydroxylamine, dissolved in methyl alcohol. Both salts crystallise well, but when re-crystallised from methyl alcohol or from water, gradually lose hydroxylamine. The trihydroxylamine salt is the more stable, and may be preserved unchanged in dry air. Both salts are acid to litmus. All attempts to obtain the normal salt $(\text{NH}_3\text{O}\cdot\text{HI})$, by direct and indirect methods, have failed; its solution is very unstable and rapidly decomposes, iodine being liberated.

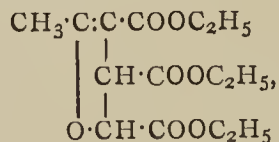
42. "*An Analysis of the Water from the Dropping Well at Knaresborough, in Yorkshire.*" By B. A. BURRELL.

The history of this remarkable spring is noticed at some length, from which it appears that its petrifying qualities were known in 1534.

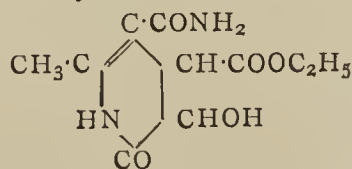
A complete analysis has now been made. The total solids amount to 162.435 grains per gallon, of which 114.37 grains are calcium sulphate, 25.48 calcium carbonate, and 17 magnesium sulphate. Traces of manganese and strontium were found.

43. "*Contributions to the Knowledge of Ethylic Acetoacetate. Part I. Acetonylmalic Acid.*" By S. RUHEMANN, Ph.D., M.A., and E. A. TYLER.

By the action of the sodium derivative of ethylic acetoacetate on ethylic chlorofumarate the authors find that the two stereoisomeric ethereal salts of the acetoconitic acids are not formed, but that in both cases one and the same compound of the formula,—



is formed, which is to be regarded as ethylic methylidihydrofurfurantricarboxylate (b.p. 188—189°, under a pressure of 15 m.m.). This constitution is supported by the chemical and physical properties of the substance. Ammonia reacts with the ethereal salt, forming a compound, which most probably has the formula,—



(m. p. 195°), whilst in the hydrolysis of the furfuran derivative, brought about by alcoholic potash, acetonylmalic acid,—



(m. p. 145—146°), is produced.

(To be continued).

NOTICES OF BOOKS.

Water Analysis. A Practical Treatise on the Examination of Potable Water. By J. ALFRED WANKLYN and ERNEST THEOPHRON CHAPMAN. Tenth Edition. Revised and partially re-written by J. ALFRED WANKLYN, M.R.C.S., Corresponding Member of the Royal Bavarian Academy of Sciences (1869). London: Kegan Paul, Trench, Trübner, and Co. (Ltd.). 1896. Pp. 200.

PROF. WANKLYN'S treatise on the sanitary examination of potable waters is universally—and we may say on the whole favourably—known to sanitarians and analytical practitioners, and has appeared in French and German versions. As regards the process itself, little alteration has been made from the previous editions. The determination of the specific gravity of samples of water with the precautions now given will be recognised as a useful addition. No directions for the microscopical and bacteriological examination of waters have been given, the author holding that if the water is shown to be "dirty" by chemical examination, the failure to discover anything very alarming by a bacteriological examination should not justify its recommendation, whilst if it belongs to "the class of exquisitely pure waters" no bacteriological results are possible.

Mr. Wanklyn still attaches no especial value to a search for phosphates. But we must not infer—as has been erroneously done—that he ignores their presence in sewage, industrial waste waters, drainage, &c. His attention in this volume is confined mainly to potable waters. The possible presence of poisonous metals—we fear a growing evil—is very carefully considered. Chromium compounds, which may easily find their way into sewage, or even into potable waters, in districts where the dyeing, tissue-printing, and colour-making industries flourish, are not here overlooked, as has been too often the case in works on sanitary chemistry. The polemical matter, which in former editions was somewhat too prominent, has been very greatly reduced. But the most satisfactory feature in the edition before us will be found in the working details and practical hints which the experience of a quarter of a century has enabled the author to supply. On this account the work will be found highly valuable, even to those many analysts, medical officers of health, &c., who are fully acquainted with the broad outlines of the method as given in the earlier editions. Prof. Wanklyn considers—very justifiably—that lead in drinking-water, even to the extent of $\frac{1}{10}$ th grain per gallon, is dangerous, and should warrant its rejection as a municipal supply.

Elementary Practical Chemistry. A Laboratory Manual for Use in Organised Science Schools. By G. S. NEWTH, F.I.C., F.C.S., Demonstrator in the Royal College of Science, London; Assistant Examiner in Chemistry, Science and Art Department. London, New York, and Bombay: Longmans, Green, and Co. 1896. Crown 8vo., pp. 283.

WHAT are "organised schools"? A school without organisation is something difficult to conceive, whether its object be Science or word-mongering. But perhaps the term may have some special meaning familiar to the officials of the "Department."

"Formerly," we are told in the author's preface,

"students were taught chemistry in the lecture-room, the knowledge so gained being supplemented by a minimum amount of practical work." This is perfectly and lamentably true. But the tendency to make the student, from the very beginning, an investigator, was manifest in the teachings of Justus Liebig, and has been carried out in every German University long before it could find expression in any Syllabus of the Science and Art Department.

The experiments here prescribed are well selected for the purpose of making the student an observer, and of training him to draw accurate conclusions from the phenomena which he observes. Hence Mr. Newth's work, and the course of study therein laid down, will be well worth adoption in any Science school, even if it has the peculiarity of not being "organised."

CORRESPONDENCE.

ON A

MECHANICAL ACTION EMANATING FROM THE CROOKES TUBE ANALOGOUS TO THE PHOTOGRAPHIC ACTION DISCOVERED BY RÖNTGEN.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS of Feb. 28th (vol. lxxiii., p. 98) I notice an article with the above heading, by MM. Gossart and Chevalier. The article claims the discovery of a "new" force, manifesting mechanical action, and details an elaborate series of experiments with this new force, and promises more to follow. Doubtless the fundamental experiment of the article has long ago been observed by most, or all, users of Crookes tubes who had at hand also a "radiometer." The explanation of all that was observed by MM. Gossart and Chevalier is, I think, very simply found in electrostatic induction. Early in February, when I first set up a Crookes tube for X ray experiments, I observed that the radiometer had a decided tendency to a fixed position of the vanes; that the azimuth of this position changed on interposing an object *unsymmetrically* between the two tubes; that the vanes could be made to rotate in *either direction* by waving them around with a magnet, the finger, or other object—but the magnet was no better than the hand. It was, of course, *easier* to get continuous rotation in the *forward* direction of the radiometer, because the electrostatic induction and proper heat radiation then conspired, while they were opposed in the opposite case. I tried three tubes in order to thoroughly satisfy myself of the electrostatic nature of the force. One was a radiometer with mica vanes, the faces alternately blackened; a second was the same, except that the vanes were of aluminium; the third tube was the Crookes tube similar in appearance to a radiometer, except that all the faces of the vanes were bright, and it was provided with terminals; the vanes themselves to be made the kathode, in order to show "the mechanical effect of the reaction—or kick—of the charged molecules flying from the kathode." All the tubes presented the same general phenomena, about the only difference being that the last tube described, in the absence of any "radiometer" effect, would rotate in either direction with *equal* facility. When one can take off sparks from the Crookes tube in action, and even from objects near by, there is no need to invent a "new force" to affect a delicate radiometer vane.—I am, &c.,

JOHN DANIEL.

Vanderbilt University, Nashville,
Tenn., U.S.A.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Journal für Praktische Chemie,
New Series, Vol. lii., Part 16.

Our Knowledge of Flame.—M. Teclu.—This paper—a continuation, and which is not yet completed—requires the five accompanying figures. Concerning the colour of flames, the author remarks that, besides the luminous action of the ignited carbon liberated, we distinguish the primary colours yellow and blue, though not in a decided state of purity, from which, since the yellow occurs reddish, the mixed colours violet and green are produced in various shades; the yellowish red tone of colour is due to the hydrogen flame, and the bluish colour to the flame of carbon monoxide. These flames interpenetrate each other. The violet colouration of the margin of the flame is produced by the reddish tone of the hydrogen flame and the bluish tone of the carbon monoxide flame.

Researches from the Organic Laboratory of the Technical High School of Dresden.—E. von Meyer.—These researches include (III.) a paper on the "Action of some Diazo-compounds upon Cyanacetic ethylester," by B. Marquardt. This paper is not suitable for abridgment.

Compound Metallic Bases.—N. Kurnakow (Treatise second).—This paper, also, is not capable of abstraction.

Zeitschrift für Anorganische Chemie,
Vol. x., Parts 1 and 2.

Re-determination of the Atomic Weight of Zinc.—Theodore W. Richards and E. Folger Rogers.—The mean value found, assuming $O=16$, is $Zn=65.404$; if $O=15.96$, then $Zn=65.240$; and if $O=15.88$, then $Zn=64.913$. A part of this memoir has already appeared in the *Proceedings of the American Academy*.

Note on the Crystallisation of Bromine.—Henryk Arctowski.—Bromine obtained from solution in carbon disulphide by refrigeration below its point of saturation forms a heap of fine crystalline needles. Bromine obtained by refrigeration in a test-tube showed, on comminution, a distinct crystalline fracture and no striated surfaces. The lustre is not so decidedly metallic as that of iodine.

Crystallography of Mercurial Chloride.—Henryk Arctowski.—This paper requires the accompanying figure.

New Method of Quantitative Spectroscopic Analysis.—G. and H. Krüss.

Preparation of Tin Tetrachloride in Quantity.—Richard Lorenz.—This paper requires the accompanying figure.

Molybdenum Hydroxyl Chloride.—Ad. Vandenbergh.—This paper cannot be usefully reproduced without the four accompanying illustrations.

Determination of Phosphoric Acid by the Molybdenum Method.—H. Neubauer.

Study of Certain Potassium Fluorides and Oxyfluorides.—G. Marchetti.—The author obtains a normal fluoride containing no crystalline water, TiF_6K_2 , which on re-crystallisation from pure water is converted into $TiF_4.2KF.H_2O$. He also obtains molybdenum oxyfluoride, $MoO_2F_2.2KF.H_2O$ and $WO_2F_2.2KF.H_2O$. In these experiments he determines the fluorine according to the method of Penfield (CHEMICAL NEWS, xxxix., p. 179).

Conversion of Chlorine into Hydrochloric Acid.—Richard Lorenz.—The author suggests the lixiviation of ores with hydrochloric acid, after which the lixivium is concentrated and electrolysed. The anodic chlorine is

again converted into hydrochloric acid, which can be afresh used for lixiviating a proportion of ore. Little is to be found in scientific literature concerning the conversion of chlorine into hydrochloric acid by means of elevated temperatures.

Experiments for the Establishment of an Electrolytic Process for the Conjoint Production of Zinc and Lead.—R. Lorenz.—This memoir would require the insertion of the three accompanying figures. Some portions, however, describing the fractionated electrolysis of fused mixtures of metallic chlorides will be inserted in full.

Compounds of Selenium with Arsenic.—A. Clever and W. Muthmann.—The authors describe the production and properties of potassium oxyselenoarsenate, of arsenpentaselenide, potassium metaselenoarsenate, potassium sulph-selenoarsenate, sodium oxyselenoarsenate, sodium selenoarsenite, sodium sulphoselenoarsenate, potassium triselenide, and a new hydrate of sodium monoselenide.

Colour of the Ions as a Function of the Atomic Weight.—Julius Thomsen.—This journal has contained a memoir by Carey Lea on "The Relation of the Atom, the Ion, and the Molecule." The author arrives at the conclusion that the periodic system, hitherto accepted, seems worthy of rejection, as being founded upon erroneous principles," and he then proposes another system based on the colour of the ions. But the dependence of the colour of the ion upon the atomic weight appears very simple if we accept the form of the periodic system which I have published in the *Zeit. Anorg. Chemie* (vol. ix., p. 318). The dependence may be simply expressed in the following words:—"Only the ions of the mean members of the great series are coloured." The two first series, each with seven members, contain no coloured ions; the two next following, each with seventeen members, contain in each series seven to eight coloured ions (from titanium to copper, and from niobium to silver); and in the fifth series, with thirty-one members—some of them undiscovered—we find the group of the coloured ions (cerium to gold) in the middle; whilst colourless ions correspond in all the series to the exterior members.

MISCELLANEOUS.

Litmus Pencils.—We have much pleasure in giving publicity to a very useful and ingenious little appliance in the form of a "litmus pencil," shown in the accompanying woodcut. Its use is so obvious that comment is unnecessary. One half is red, and the other half blue; it only needs a couple of point protectors to make it



complete, and we have no doubt but that it will soon in great measure supersede the old form of books. To medical men it will certainly be a great boon, as it can be carried in the pocket and contains a practically inexhaustible supply of litmus always ready. Messrs. Christy and Co., of Lime Street, E.C., are the sole agents for England.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, the 7th and 8th days of May, 1896, commencing each day at 10.30 a.m. The following is a list of the Papers that are expected to be read and discussed:—"On the Rate of Diffusion of Carbon in Iron," by Professor W. C. Roberts-Austen, C.B., F.R.S. (Member of Council). "On some Alloys with Iron Carbides," by J. S. de Benneville (Philadelphia). "On Mond Gas as applied to Steel-making," by John H. Darby (Brymbo).

"On Hot Blast Stoves," by B. J. Hall (Westminster). "On the Hardening of Steel," by H. M. Howe (Boston); adjourned discussion. "On the Introduction of Standard Methods of Analysis," by the Baron Hanns Jüptner von Jonstorff (Neuberg, Austria). "On the Production of Metallic Bars of any Section by Extrusion," by Perry F. Nursey (London). "On Mr. Howe's Researches on the Hardening of Steel," by F. Osmond (Paris). "On the Treatment of Magnetic Iron Sand," by E. Metcalf Smith (New Zealand). "On the Making of the Iron Ores of Oxfordshire," by E. A. Walford, F.G.S. (Banbury).

Penetration of Gases into the Glass Sides of Crookes Tubes.—M. Gouy.—If we heat with the blow-pipe glass from a Crookes tube which has been in use for some time, it is seen to take a dull aspect, which at first makes us believe in denitrification. The alteration is confined to the interior surface of the tube; it is so much the more marked as the glass has received a more intense cathodic irradiation, and does not exist in those portions which have not been exposed. The microscope shows that this mat layer is especially formed of a multitude of gas bubbles, which are in the interior of the glass, but near its surface. On heating further these bubbles coalesce, increase in bulk, and finally become visible with the lens, or even to the naked eye. Thus glass which has been exposed to intense cathodic rays disengages numerous bubbles of gas when softened by heat. This phenomenon is not produced in any other case. It seems that the cathodic rays cause the gases of the tube to penetrate into the glass, where they remain occluded until set at liberty by the softening of the glass. These observations have been made with four tubes of glass somewhat different; one of them showed abundant bubbles only in the portions which had been most exposed to the cathodic rays.—*Comptes Rendus*, cxxii. p. 775.

Determination of Mercuric Salts by means of Sodium Peroxide.—Dr. R. C. Schuyten (*Chemiker Zeitung*).—I have previously stated (*Akad. Proefschrift*, Ghent, 1894) that sodium peroxide—a substance with oxidising properties—is capable of reducing sublimate to metallic mercury. Upon this behaviour I founded a method for the determination of mercuric salts which has the advantages of being quickly executed and of yielding accurate results. I have examined the following compounds with good results:—Mercuric chloride, mercurous chloride, mercuric sulphate, nitrate, and oxide (red). These substances, both in solution and suspended in water, are reduced first to yellow oxide, and then completely to metallic mercury. In the solutions filtered off from the precipitates no precipitation was caused by hydrogen sulphide. The determination was carried out

as follows:—In a porcelain capsule, which can be closed by a funnel, with a pipe bent at right-angles, the weighed substance is closed with a sufficiency of water. The sodium peroxide is then added by degrees until no further precipitate appears. The capsule is then closed with the funnel, and the liquid gently heated until the vapours condense in the tube; it is then allowed to cool, the funnel is well rinsed out, the metallic mercury is placed on a filter and weighed. During drying, the filter must be covered with paper, and the exsiccator placed in the dark at a low temperature. With sublimate purified by re-crystallisation I have obtained the following results:—Found, Hg, 73.54, 73.61, 73.41 per cent; calculated quantity, 73.92. In this case the halogen can be liberated by Volhard's method in the neutralised filtrate. Under the above conditions vermilion is not decomposed, even on ebullition, but this is the case in the organic mercurial addition products.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 13th inst., Sir James Crichton-Browne presiding. The following were elected Members:—Robert James Forrest, Major-General Sir Francis Grenfell, K.C.M.G., K.C.B., and M. W. Zambra.

MEETINGS FOR THE WEEK.

MONDAY, 27th.—Society of Arts, 8. (Cantor Lectures). "Applied Electro-Chemistry," by James Swirburne. Medical, 8.30.
TUESDAY, 28th.—Royal Institution, 3. "Child-Study and Education," by Prof. James Sully, M.A. Institute of Civil Engineers, 8. Photographic, 8. Medical and Chirurgical, 8.30.
WEDNESDAY, 29th.—Society of Arts, 8. "Fruit Drying or Evaporation," by Edward W. Badger. British Astronomical, 5. Geological, 8.
THURSDAY, 30th.—Royal, 4.30. Royal Society Club, 6.30. Institute of Electrical Engineers, 8. Royal Institution, 3. "Recent Chemical Progress," by Prof. Dewar, F.R.S.
FRIDAY, May 1st.—Royal Institution, 5. (Annual Meeting). At 9, "Chronographs and their Application to Gun Ballistics," by Col. H. Watkin, C.B. Geologists' Association, 8. Quekett Club, 8.
SATURDAY, 2nd.—Royal Institution, 3. "The Vault of the Sixtine Chapel," by Prof. W. B. Richmond, R.A.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1901.

2 MAY 96

ON THE DIFFRACTION AND THE POLARISATION OF THE RÖNTGEN RAYS.

By G. SAGNAC.

I. To obtain real images of a luminous slit with a grating by transmission at equal intervals, we place it in front of a real image furnished by a converging sheaf of rays. We cannot do this with the Röntgen rays, which diverge on the exterior of a Crookes tube, and for which we have no lenses. To obtain real images of a slit I have diaphragmed the entrance into a large camera by a second slit, behind which is placed the grating.

I used a grate of $\frac{1}{10}$ m.m., constructed by M. Gaiffe, with platinum wires of nearly $\frac{1}{10}$ m.m. in diameter. The lower part of a luminous sheaf, defined by two metallic slits at the distance of 7.5 c.m., passes below the metallic mounting of the screen, and forms—on ground glass of the camera at 35 c.m. beyond the screen—a real image of the first slit. The upper part of the same sheaf traverses, at 2.5 c.m. behind the second slit, the screen placed at the incidence of 45° , which here augments the deviations and the intensities of the diffracted rays. These latter add to the direct image so many diffracted images, four of which are especially very distinct. These five images of the first slit, supposed to be rather narrow ($\frac{1}{2}$ m.m.), reinforce themselves by being partially superimposed, and form thus an image of a fluted aspect, broader by about 7 m.m. than the lower image without diffraction.

We regulate the parallelism of the edges of the slits among themselves and with the wires of the grating. For this purpose we realise the maximum distinctness of the diffraction fringes of the second slit illuminated by the former, rendered fine, then that of the shadows of the wires of the grating given by the second slit, rendered fine in its turn, the former being enlarged up to 1 m.m. We then enlarge the second slit until the shadows of the wires are seen to disappear.

For the source of light illuminating the slit we substitute a Crookes tube, and for the plate of ground glass a frame charged and closed. We have obtained a very well-defined proof.* We must seek to recognise in it the diffraction of a greater breadth of the upper image. If this image exceeds the lower image in breadth, such excess is certainly not more than $\frac{1}{2}$ m.m. It differs from the lower image solely by a width of 2 m.m. on each margin, where it presents seven appearances of fringes; but these apparent fringes correspond to the juxtapositions of the margins of the first slit given by the transparent intervals, to which the second slit limits on the screen the pencil of rays coming from each margin of the first slit.

Further, we substitute for the Crookes tube the flames of common salt, on exposing for about an hour with an open frame, and, using an orthochromatic plate (sensitive to yellow and green), we obtain a proof differing from the former by a fluted upper image enlarged by more than 7 m.m., even if we neglect the most intense parts of the margins. Now the appearances of five fringes of the former proof re-occur here between the broader flutings, as well in the last diffracted images as on the margins of the central image, and the simple nature of the light em-

ployed does not permit them to be considered as due to diffraction by the grating; they are certainly phenomena of shadows just explained. These same images of the margins of the first slit are certainly not very visible on proofs obtained with an open frame, either with ordinary gas-light or with the light of a Crookes tube, on account of the complication which the nature of the sources employed impresses on the diffracted flutings, especially if the sensitive plate is orthochromatic.

The expansion of the copper sheaf by diffraction, if it exists at all, does not exceed $\frac{1}{2}$ m.m. or scarcely $\frac{1}{4}$ m.m. Now an expansion of $\frac{1}{2}$ m.m., fourteen times less at least than that given by the light of the D ray, would correspond to a wave-length of 0.04μ .

This enables us to conclude that the Röntgen rays which have acted on the sensitive plate through the wooden shutter of the frame do not possess wave-lengths exceeding a hundredth of a micron.

II. Are the Röntgen rays connected to a vector either longitudinally or transversely, and in the latter case how can they be polarised?

We cannot at present dream of polarising them by reflection, nor by refraction, nor doubtless by diffraction. Emission and diffusion might perhaps be tried. It is in any case simpler to attempt to polarise them by absorption. Let there be two crystalline plates, near to each other in thickness, parallel to the axis, superimposed with their axes parallel. Let us divide the surface of the upper plate in two halves, and cause one of them to turn by 90° . The system of the plates realises at once the analogue of the crossed tourmaline and of parallel tourmalines. With a monochromatic light the amplitude r becomes, when issuing from a plate, for the components perpendicular and parallel to the axis, respectively o and e , which differ if there is dichroism. The region of the principal parallel sections allows an intensity to pass, the excess of which over that of the other region is measured by $(o^2 - e^2)^2$.

Otherwise for the differences $(o - e)$ possibly of different signs, relative to different wave-lengths, the corresponding differences of intensity accumulate always in favour of the region where the principal sections are parallel.

I have sought if the effect is produced with the Röntgen rays when such system of three plates are arranged on the double black paper which covers the sensitive plate. The time of exposure was increased to several hours. The proofs obtained with the desirable intensity have not revealed a sensible dichroism.

Substances used.	Quartz.	Spar.	Brown Tourmaline.	Mica.	Potassium ferrocyanide.
	M.m.	M.m.	M.m.	M.m.	M.m.
Thickness of each plate	0.03	0.4	0.5	0.2	0.4 to 2

One precaution is indispensable to eliminate the influence of a small difference of nature, such as occurred in the tourmalines: we cause each of the two upper half-plates to turn on the spot by 90° , so that the regions of the principal parallel sections and of the crossed sections are mutually interchanged. A difference of intensity due to dichroism ought, in its displacement, to follow the parallelism of the principal sections. Now the very small difference of intensity perceived with the tourmalines always persisted in the same half-plate.

If the method admits of so easy a check, and is found independent of the complexity of the radiations employed, it is unfortunately not very sensitive. We see readily, in the case of light, that to detect a difference, e.g., of $1/10$ th between unity and the relation $\frac{o}{e}$, the photograph must be able to show a relative difference of $1/50$ th between the luminous intensities which act upon two contiguous regions, which far exceeds that which may be hoped.

We cannot therefore derive from these negative experiments on dichroism an argument of great value in favour of the hypothesis of a longitudinal vector. They supply

* The Crookes tube manufactured by M. Chabaud has acted for eleven days, on an average five hours daily, without becoming sensibly weaker, and becoming heated less and less rapidly.

merely a further distinction between the X rays and the luminous rays which we know. — *Comptes Rendus*, cxxii., p. 783.

A CONDITION OF THE MAXIMUM OF POWER OF CROOKES TUBES.

By JAMES CHAPPUIS and E. NUGUES.

THE power of a Crookes tube, actuated by a Ruhmkorff coil with a Foucault interrupter, does not increase for one and the same intensity of current, measured in the closed inductor, in the same time as the number of interruptions.

We have measured this power with the electrometer of Hurmuzescu placed at various distances, and caused the number of interruptions to vary from 3 to 50, by the displacement of an additional weight on the oscillator. The following numbers show that for the coil experimented with there is a maximum reached near 10 interruptions :—

Number of interruptions.	Time of fall.	
3	27	47
6	23	—
10	20	24
25	30	34
50	37	42

The recent experiment on the emission of rays having a photographic power by means of fluorescent substances have led us to think that the visible fluorescence of the glass on the passage of the discharge may be followed by a kind of invisible fluorescence prolonging the photographic action. To verify this hypothesis we have made the following experiment :—

On the stem of the oscillator we fixed a thick plate of copper in which there had been made a slit of about 1 m.m. in width by 12 m.m. in height; a sensitive plate was placed behind and parallel to it, at the distance of 1 m.m. the source of light fitted with a diaphragm of 8 m.m. on the other surface of the metal plate at the distance of 1.6 c.m.

When the Foucault oscillator is set in motion, the rod carries with it, in its oscillatory movement, the slit over a course of 4 c.m., and at each double oscillation there is produced a fluorescence. We have caused the speed of the oscillator to carry from 3 to 20 interruptions per second, and the time of exposure from 1 to 30 minutes.

If the useful fluorescence is instantaneous, like the discharge which produces it, we ought to obtain a distinct image of the slit; if, on the contrary, it lasts a certain time, we ought to obtain a band giving at each point an indication of the photographic power of the tube at a corresponding instant.

In all cases we have obtained a distant image of the slit and of the movable plate; it would therefore be sufficient to convince ourselves of the inaccuracy of our hypothesis, to photograph the stem of the oscillator in movement; it gives, in fact, on our proofs a shadow with very definite edges.

We deposit a proof obtained by 36,000 passages of the slit.

The power of the tube is hence instantaneous, like the discharge which induces the fluorescence.

It seems to follow, from this experiment, that the power of the tube should be proportional to the number of the discharges; but, on the other hand, the length of the sparks which strike between the two bulbs of an exciter falls from 21 to 5 c.m. when the number of interruptions varies from 3 to 50.

There are then two phenomena which vary inversely, and which we must take into account for the production of the maximum power of the tube.

This maximum depends on the self-induction of the

induced coil, and the conditions necessary for its production vary, for one and the same current measured in the closed conductor, with the coil employed. Experiment alone permits it to be determined. — *Comptes Rendus*, cxxii., p. 810.

RESEARCHES ON THE EARTHS CONTAINED IN MONAZITE SANDS.

By P. SCHUTZENBERGER and O. BOUDOUARD.

WE have the honour of communicating to the Academy the continuation of our researches on the earths contained in the monazite sands, and especially in the salts, the double potassium salts of which are soluble in water saturated with potassium sulphate.

After treating the powdered mineral in heat with concentrated sulphuric acid, and eliminating the excess of sulphuric acid, the aqueous solution is concentrated in the water-bath. Then are separated, in heat, crusts of rose-coloured crystals, chiefly consisting of sulphates of the cerium group. The mother-liquors of the crystals are saturated with neutral potassium sulphate, which occasions the precipitation of the rest of the cerium bases, carrying down with them a fraction of the yttrium bases. We isolate the latter by repeated precipitation of the sulphates with potassium sulphates, until the liquid floating above the crystalline deposit of double sulphates no longer contains earths precipitable by ammonia.

The yttrium earths are freed from alkali by repeated precipitation with ammonia, and subsequent washing. They are then converted into nitrates, after having been previously formed into oxalate.

The mean atomic weight of the metals of the yttrium earths thus isolated is between 105 and 106, if we do not include those which are mechanically carried down by the first precipitation of the double potassium sulphates, and which give a higher atomic weight, near 126.

The mixture of the nitrates (105 to 106) was submitted to fractionated decompositions at a temperature of 310° to 315°. The operation is effected on a cylindrical capsule of platinum, with a flat bottom, plunging into a bath of potassium and sodium nitrates in equal equivalents. The melted nitrate begins by giving off nitrous vapours, then it thickens, and is finally converted into a solid crystalline mass, solid at 310°. When all decomposition has ceased it is allowed to cool, and treated with hot water. The mass is separated into an insoluble sub-nitrate, representing about a fourth of the product employed, and a soluble portion of neutral nitrate. The latter is evaporated to dryness and submitted to the same treatment, and gives a further insoluble sub-nitrate and neutral nitrate. The sub-nitrates thus obtained are washed with hot water and transformed into sulphates, and we determine for each the corresponding atomic weight by ignition to bright redness, sufficiently prolonged.

We find (1) that the proportion of sub-nitrate separated diminished each time; (2) that the corresponding atomic weights decrease from 108 to 102, and then finally to 96, the lower limit, which has not yet been passed.

We have applied to the different fractions of the sub-nitrates obtained a second method of separation, founded upon the fractionated crystallisations of the sulphates. We evaporate the solution of the sulphates in the water-bath in a porcelain capsule, and separate the successive crystallisations which are formed.

We may concentrate the solution until the larger part of the product is deposited, isolate the relatively small part of the mother-liquid, and re-commence the same operation with the crystals. The atomic weight of the crystals obtained by the complete evaporation of these mother-liquors has for some time a value close upon 97 to 98, and then rises progressively.

Lastly, we have still made use of the method of frac-

tionated precipitation by ammonia, but only to check certain of our results.

By proceeding thus, and applying successively and alternately the procedure with the nitrate, and that with the sulphate, we have finally, and after many attempts, succeeded in isolating a colourless earth, the atomic weight of which is no longer appreciably modified either by fractionation with the nitrate, or with the sulphate, or by partial precipitation with ammonia. The fixed atomic weight at which we have arrived is very close upon 102 (101.95 and 102.4).

Can this earth be divided by other procedures? This is what ulterior researches must establish.

From the totality of our researches we believe that we may equally conclude that by following the same course we shall arrive at other fixed terms, above and below 102, and equally resisting the procedures of separation employed.—*Comptes Rendus*, cxxii., p. 697.

ON
NUMERICAL RELATIONS EXISTING BETWEEN
THE ATOMIC WEIGHTS OF THE ELEMENTS.

By M. CAREY LEA.

IN the first part of a paper on the Ions it was shown that the elements were divisible into three great classes; those whose ions were always colourless, those whose ions were always coloured, and a smaller class whose ions were coloured at some valencies and colourless at others.*

It was also shown that the first class, those whose ions were always colourless, can be arranged in vertical lines so that the horizontal lines contained each a natural group. Also that the elements having both coloured and colourless ions were much more closely allied to these than to the group having always coloured ions. This last named class does not divide into groups at all, but forms series with the atomic weights immediately following one another.

Therefore as long as an element has any colourless ions it really seems to belong to the class with the ions all colourless. So much so that when the first class is tabulated the members of this transitional class find vacant spaces into which they naturally fall. To make this clear and to elucidate what follows I here reproduce Table II. from the first part in a condensed form.

I.	H 1	F 19	Cl 35.5	Br 80	J 127	—
II.	Li 7	Na 23	K 39	Rb 85	Cs 132	—
III.	—	—	Ca 40	Sr 88	Ba 137	—
IV.	—	—	Sc 44	Y 90	La 139	—
V.	—	—	Ti 48	—	—	—
VI.	—	—	V 51	Nb 94	Ta 183	—
I.	—	—	—	Mo 96	W 184	—
II.	—	—	Cu 63	Ag 108	Au 196	—
III.	Be 9	Mg 24	Zn 65	Cd 112	Hg 200	—
IV.	B 11	Al 27	Ga 69	In 114	Tl 204	—
V.	C 12	Si 28	Ge 72	Sn 118	Pb 206	Th 234
VI.	N 14	P 31	As 75	Sb 120	Bi 208	—
	O 16	S 32	Se 79	Te 125	—	—

In the case of some few elements it has not been easy to find published data sufficient to determine with absolute certainty the colour of the ions. Further study of this subject has led me to make a slight change in reprinting the above table. I had previously classed the metal cerium as transitional. The ceric ion is undoubtedly coloured, but as to the cerous iron there is some uncertainty. Its compounds are nearly colourless, but as they exhibit a slight red tinge the ions may perhaps be coloured. It therefore seems better in this uncertainty to place cerium alongside of the other members of its

group; it is therefore omitted from the above table. Also in the paper just referred to gold was placed amongst the elements having coloured ions only. The auric ion is certainly coloured, but about the aurous ion there is some doubt; the oxides and the haloids are coloured, but as they are insoluble they give no positive information. It appears, however, that when aurous chloride is dissolved in sodium chloride it yields a colourless solution from which colourless crystals are obtained. Various other double salts form both colourless solutions and colourless crystals. The following are examples:—Ammonium aurammonium sulphite, sodium aurothiosulphate, potassium aurocyanide, &c. ("Roscoe and Schorlemmer," 1st Ed., ii., pp. 380-1).

As it seems characteristic of the soluble salts to be colourless, I conclude that gold must be considered as having both coloured and colourless ions. It is therefore a transitional element and finds its place in the above table, where elements of that class appear in italics. It is, however, interesting to observe that just as these two metals cerium and gold are at the very limiting point between two classes, so there are spaces open for them in each of these classes, a circumstance that can hardly be fortuitous.

Table of Differences.

If the respective numbers of the first column in the preceding table be each subtracted from the corresponding number of the second column, the second column from the third, and so on, we obtain a series of differences which are given in the table below.

18	16.5	44.5	47
16	16	46	47
—	—	48	49
—	—	45	49
—	—	44	88
—	—	—	88
—	—	45	88
15	41.3	46.7	88
16	42	45	90
16	44	46	88
17	44	45	88
16	47	46	—

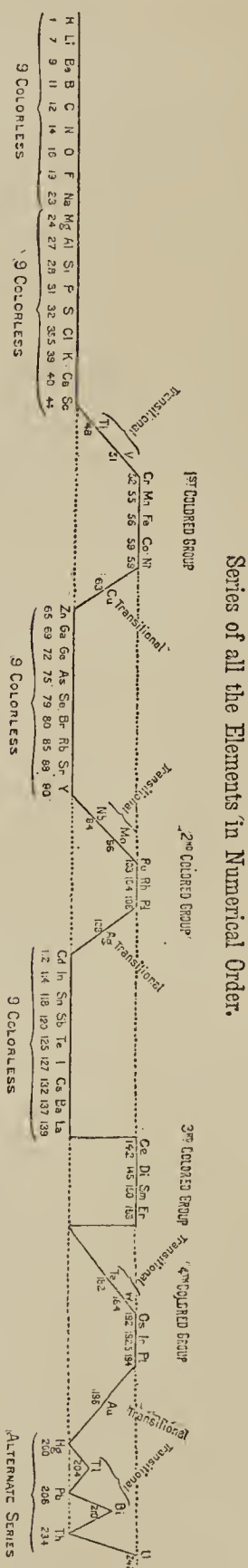
It has been remarked, I think as far back as the time of Dumas, that differences of 16 between the atomic weights frequently presented themselves, and occasionally differences of 45 or thereabouts. But these were scattered cases. In the above table of differences *all* the elements are represented with the exception of the comparatively small group having ions always coloured. As has been already said, this last group of elements, having nothing in common with other elements, cannot be classed with them, and will probably be found, when we know much more than we do now, to have a wholly different constitution.

There are several things worthy of remark in the above table. It will be seen that the differences at first approximate to 16. Then comes a long set of differences, twenty in number, beginning with 41.3, and gradually, but not regularly, increasing to 49. The remaining differences are all exactly 88, with one exception of 90; but as this is the difference between two metals of which comparatively little is known, and whose atomic weights cannot be considered as being accurately fixed (indium and thallium) it is quite probable that this exception may hereafter disappear.

It should be remarked that when the set of differences approximating 16 is once left behind, this difference does not reappear in a single case. The same is true of the differences averaging 45: this class of differences does not once reappear when 88 is reached.

For some time past it has been believed that the oxygen group does not end with tellurium, but contains still another member with a higher atomic weight. It will be observed that in both the above tables there remains a

* *American Journal of Science*, June, 1895. The second part will appear shortly.



space for such an element. Its atomic weight should exceed that of tellurium by the difference 88, and should therefore be 213. Finally, it may be said that the blanks in the table of differences are due to corresponding blanks in the table of atomic weights.

The change just mentioned in the classification of cerium and of gold makes a slight change in the table representing the whole range of elements in series. I therefore reproduce this table as corrected.

It will be observed that all the elements having only colourless ions appear on the base line. The elements having ions always coloured appear on the upper line parallel to the base line. The transition elements appear on the inclined lines.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 193).

CHAPTER XI.

CHEMICAL RESEARCHES ON THALLIUM, AND ITS TRIOXIDE, HYDRATE, CHLORIDE, BROMIDE, IODIDE, NITRATE, CARBONATE, AND THALLOUS SULPHATE.

THE spectrum of thallium having been the subject of some discussion, I thought I ought to submit to a fresh examination the preparation and properties of the metal and its principal compounds. For this research I was fortunate in having put at my disposal:—1st, about 100 grms. of sulphate of thallium, prepared by the late M. Lamy during the course of his work on this metal; 2nd, some metallic thallium and carbonate of the same, through the kindness of Mr. Crookes, and prepared by himself. Lastly, I obtained some of the metal as prepared on a large scale in a chemical manufactory.

On the Sulphate of Thallium prepared by the late M. Lamy.—I started this research on sulphate prepared by the late M. Lamy. Having detected in it the presence of small quantities of sulphate of silver, of calcium, iron, sodium, and silicon, I had recourse to the following treatment to effect their separation:—

Pure ammonia was added to the boiling and saturated sulphate solution; it was kept boiling for several minutes in a large platinum dish, and then filtered. After the ferric hydrate was separated, the liquid was again treated with ammonia; kept boiling for several minutes, and filtered.

Traces of ferric hydrate being left a second time on the filter, I added ammonia a third time, and again boiled and filtered it.

After the iron was quite eliminated, I boiled the dilute solution, and added dissolved sesqui-carbonate of ammonium, little by little, to precipitate the calcium.

The slightly ammoniated liquid was filtered after cooling, to separate the carbonate of calcium mixed with a small quantity of crystallised thallos sulphate.

I then evaporated to dryness the clear sulphate solution, to drive off the excess sesqui-carbonate of ammonium. The salt was dissolved in a saturated solution of sulphuric acid. The sulphuric solution was coloured brown.

When left alone in a platinum vessel under a bell-jar, it became violet-coloured, then quite colourless and clear, by depositing a slight deep red precipitate, consisting of sulphides of thallium and silver.

The clear liquid, when decanted, smelling strongly of sulphurous acid, was nevertheless added to a quarter of its volume of the sulphurous solution, and again left to itself in a closed vessel. After twenty-four hours it was quite colourless, and had no deposit.

A neutral solution of thallos sulphate, from which the metals capable of being precipitated by sulphurous acid have been eliminated, is therefore not decomposed by this acid, contrary to the general opinion.

The deep red precipitate mentioned above, having been collected on a filter and washed with a saturated solution of sulphurous acid, was left to itself in damp air under a bell-jar. It was transformed by oxidation, chiefly into thallos sulphate, and after washing left as residue a very small quantity of sulphide of silver.

The solution of the products of oxidation of the deep

red precipitate, when added to sulphurous acid and water, was neither coloured nor clouded after twenty-four hours in a closed vessel. This solution consisted entirely of neutral thalious sulphate, unchanged by a sulphurous acid solution. These facts prove that neutral thalious sulphate is only precipitated by sulphurous acid when it is associated with a metal capable of being thus transformed into an insoluble sulphide.

I evaporated the thalious sulphate solution to dryness in a platinum vessel, and heated the white residue to a dull red heat to destroy the small quantity of sulphate of ammonium, and make the silicic acid in it soluble.

The sulphate imparted the thallium colour to a hydrogen flame, and spectrum analysis of this flame immediately showed the sodium and thallium lines, *but no others*.

Four successive crystallisations were required before the spectrum of thalious sulphate could be seen without the sodium line. I did not conclude from this that there was no sodium present; I have enlarged upon this point elsewhere. When left in air under a bell-jar it showed the sodium line very strongly after a few days.

Crystallised thalious sulphate is colourless, and remains so even when exposed to direct sunlight in air.

I used this salt to prepare some of the pure metal, and also its trioxide and chloride.

I electrolysed an ammoniated solution of the sulphate in order to obtain at once the pure metal and its trioxide.

My reasons for using an ammoniated solution were as follows:—

When a saturated aqueous solution of sulphate in a platinum dish is subjected to electrolysis, it deposits thallium on the negative electrode in the platinum, and coats the positive electrode with hydrate or brown or black oxide. Mr. Crookes was the first to notice this fact. I found that, at the commencement of electrolysis, the ratio between the weight of thallium deposited in a metallic state and that deposited as an oxide is almost exactly as 2 to 1. This ratio quickly alters as sulphuric acid is liberated, and a time is reached when, at the negative electrode, hydrogen only is liberated, whilst the positive electrode is still being coated with black oxide. This action goes on with such regularity that when subjecting a solution of monothallic sulphate to a current, all the metal is eliminated in the form of hydrated trioxide.

Electrolysis of ammoniated sulphate, on the other hand, goes on quite uniformly. By maintaining a slight excess of ammonia in the liquid by successive additions, it deposits two parts by weight of metallic thallium to one part of thallium in the form of brown hydrate or black oxide, according to the temperature. By electrolysing ammoniated sulphate under a bell-jar full of *purified air*, thallium and its trioxide are produced, which, on spectrum analysis, fail to show the sodium line.

I made use of this last reaction to obtain directly the metal and its oxide, and to procure afresh from the oxide some sulphate and metallic thallium, by which means I could ascertain whether the sulphate, the metal, and the oxide contained a *spectroscopically identical base*.

I proceeded as follows:—Having kept part of the metal and the oxide produced, I transformed the rest of the metal, previously well washed with water, into sulphate, by attacking it with pure dilute sulphuric acid in a covered platinum vessel.

The oxide was also converted into the form of sulphate. For this purpose, after having treated it in succession with boiling water, then adding pure sulphuric acid and dilute ammonia, and finally washing it in pure water, the oxide was dissolved in a solution of sulphurous acid prepared in platinum, taking care to use an excess of acid and to keep the liquid boiling until it ceased to turn brown on the addition of ammonia,—that is to say, until the bisulphate of thallium, formed at first, was completely transformed into thalious sulphate by the excess of sulphurous acid and the action of heat. I found thus that brown

hydrate and black oxide, made by electrolysis of a sulphate, when previously treated with sulphuric acid, are soluble in an excess of a sulphurous solution, forming a perfectly clear liquid, which does not occur when the sulphate contains traces of *oxide of lead*, as it frequently does.

The sulphate solution made from the metal, and that made from oxide, had pure ammonia added to them, and were electrolysed, so as to precipitate oxide of thallium on a small dish, and metallic thallium on a sheet of platinum.

The metal and the oxide were, after being washed in boiling water, introduced into a hydrogen flame, and showed, on analysis, a thallium spectrum identical with that of the sulphate originally used, and with that of the metal and the oxide from which they were derived.

In order to be quite certain that I had made no mistake, I proceeded a third time to convert oxide into sulphate, and electrolyse the resulting sulphate. The spectrum of the metal and that of the oxide were identical. I concluded from this identity that the metal was chemically pure.

I re-converted the greater part of the metal and the oxide into sulphate by the methods above mentioned, and the latter into chloride. For this purpose a saturated aqueous solution of sulphate was added to water containing 10 per cent of pure liquid hydrochloric acid. The precipitate was washed with water containing 6 per cent of liquid hydrochloric acid, by means of a filter pump. I found it was necessary to add this amount of liquid acid to the water in order to dissolve as little chloride of thallium as possible. I continued to wash it with acidulated water until about half the precipitate was removed, without obtaining a liquid which would not cloud a solution of chloride of barium.

The precipitate therefore retained some sulphuric acid, probably in the form of thalious sulphate. The precipitate was quite white, and remained absolutely white after exposure to direct sunlight. Lamy has already noted that chloride of thallium is not altered by light. It has been stated, however, that exposure to light turns this compound greyish; I only met with this property in it when it was obtained by means of nitrate of thallium or thalious sulphate containing silver, and this is almost always the case when the salts are made from solutions which have not been treated with sulphuric acid.*

With the object of obtaining chloride of thallium free from sulphuric acid, I dissolved the precipitate in boiling water in a covered porcelain dish, and, after adding to the solution *one-sixth part* of its volume of liquid hydrochloric acid, I cooled it quickly. I repeated the solution and precipitation a second time, and obtained a granular chloride of thallium, perfectly white, *unaffected* by light, and quite free from sulphuric acid after washing it with pure water. Immediately after its preparation, or when kept under water *in a closed glass vessel*, it showed no signs of the presence of sodium. When left under a bell-jar full of dry air, it slowly occluded sodium, so that at the end of four or five days the sodium and thallium lines could both be seen. I do not conclude, from the absence of the sodium line in the chloride of thallium spectrum immediately after its production, that it did not contain a trace of sodium. I wish to make a reservation on this point, on which I shall enlarge later on.

Chloride of thallium, crystallised by cooling from a boiling solution, when stirred up with cold water, forms a liquid which is not clouded by the addition, in the cold, of concentrated hydrochloric acid.

Powdered chloride of thallium, obtained by precipitation in the cold from a solution of thalious sulphate or nitrate of thallium, by means of an excess of hydrochloric acid, when washed in succession with a 10 per cent solution of hydrochloric acid and with pure water, and

* Silver bearing chloride of thallium does not show the characteristic silver lines, whether the flame spectrum or the electric spectrum of this compound chloride be examined. The thallium line only is seen.

taken up by pure water, leaves after standing, a clear solution which is very greatly affected by the addition of concentrated hydrochloric acid.

Crystallised and powdered chlorides of thallium therefore behave, in the presence of hydrochloric acid, in a similar manner to granular and flocculent chlorides of silver.

The luminous spectrum of chloride of thallium is identical with that of the metal and its pure trioxide and sulphate.

(To be continued).

THE VOLUMETRIC COMPOSITION OF AMMONIUM CHLORIDE.

A CLASS AND LECTURE EXPERIMENT.

By D. CARNEGIE and H. WALES.

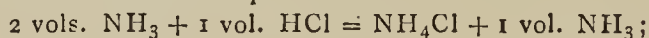
IN an elementary course of chemistry, the fact that a certain volume of ammonia combines with an equal volume of hydrogen chloride to form ammonium chloride soon presents itself for statement and experimental verification. Given a mercury trough and a good supply of mercury, there would be no difficulty in executing the required experimental proof. But even in well-stocked laboratories, mercury in sufficient quantity for the performance of mercury-trough experiments by a class, is not always at hand, and considerations of portage often preclude the use of mercury by itinerant lecturers.

The following is a description of an experimental proof of the volumetric composition of ammonium chloride which does not involve the use of mercury. It is founded on the fact that kerosene is very readily saturated by ammonia.

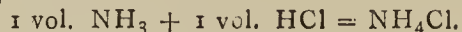
In the accompanying figure *a b* represents a glass tube of about 2 c.m. diameter and 55 c.m. length. At its upper end it is provided with a ground glass stopper, *s*, and at one-third of its length from this end is a wide-bored stopcock, *s'*. The capacity of the portion *b* of the tube, from *s'* down to a fiducial mark coincident with the level of the liquid in *c*, is exactly twice that of the portion *a*.

By downward displacement *a* is filled with hydrogen chloride at the temperature and pressure of the air in the room. The portion *b* is then filled with kerosene which has been saturated with dry ammonia, and the tube is inverted in the small glass trough *c*, which also contains ammoniated kerosene. Dry ammonia at the temperature of the room is now passed into *b*, till the kerosene stands at the fiducial mark both inside and outside the tube. On now opening the stopcock, *s'*, the gases combine, and after time has been allowed for the radiation of the heat of combination the kerosene rises to the level of the stopcock, while the portion *a* of the tube, now densely coated with a white deposit of NH_4Cl , remains filled with the excess of ammonia.

The result of the experiment is then as follows:—



or, subtracting 1 vol. NH_3 from both sides of the equation,—

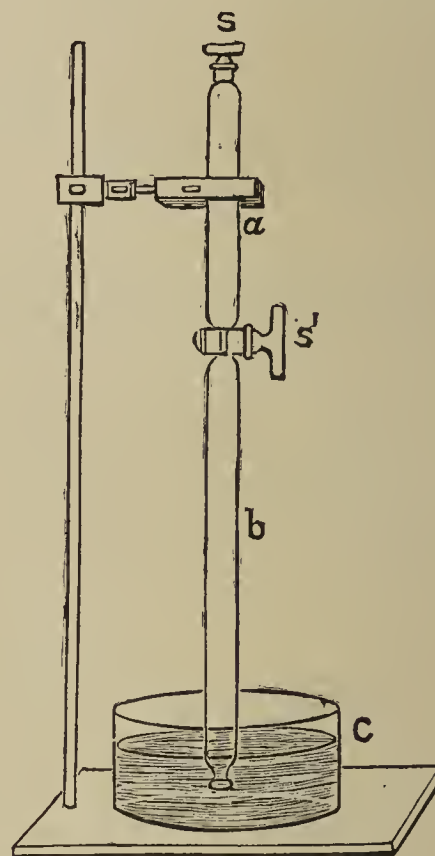


The following question may suggest itself:—Why not make *b* of the same volume as *a*, so as to get a "complete vacuum" on the combination of the gases, and therefore a complete filling of the tube with ammoniated kerosene?

The answer is to the effect that this was in fact the procedure which we at first adopted; but we found that under these conditions, the kerosene does not completely fill the tube after combination of the gases, the reason being that the ammoniated kerosene gives off its ammonia to the vacuum. This evolution of ammonia from the ammoniated kerosene does not take place to any appreci-

able extent under the partial pressure (nearly atmospheric pressure) which obtains in the case of a tube proportioned as in the figure.

We may add that the volume composition of NH_4Cl may be proved by the method described to a much higher degree of accuracy than can the statement, met with in many books on chemistry, to the effect that mercury rises



and fills a eudiometer in which electrolytic gas has been exploded. In this connection it is interesting to refer to E. W. Morley's recent paper on the combining volumes of hydrogen and oxygen. In this paper he states that he has not yet definitely determined the conditions of voltage, temperature, and dilution of acid, under which electrolytic gas has exactly the composition expressed in the symbolism $2\text{H}_2 + \text{O}_2$.

The Leys School, Cambridge.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

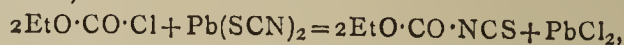
Ordinary Meeting, March 19th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 162).

44. "The Action of Lead Thiocyanate on the Chlorocarbonic Esters. Part I. Carboxyethylthiocarbimide and its Derivatives." By ROBERT E. DORAN.

In July, 1895, the existence of di-acidylthiocarbimides in solution was shown by Dixon and Doran (*Trans.*, lxvii., 565), and the present communication contains an account of the preparation of a more highly oxidised thiocarbimide. Interaction occurs between lead thiocyanate and ethyl chlorocarbonate in accordance with the equation,—



and the product was obtained by distillation under diminished pressure as a colourless highly refractive liquid, possessing a pungent fungus-like odour and the

general properties of a thiocarbimide. The following derivatives were prepared and examined:—

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5$, ab-*Carboxyethylphenylthiocarbimide*. From the thiocarbimide and aniline; pure white, apparently monoclinic tables, m. p. 130° .

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5 \cdot CH_3$, ab-*carboxyethylbenzylthiocarbimide*. By interaction with benzylaniline; colourless needles, m. p. $106.5-107.5^\circ$.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5 \cdot CH_3$, ab-*carboxyethyl-orthotolylthiocarbimide*. By interaction with *o*-toluidine; long white prisms, m. p. 152.5° .

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5 \cdot CH_3$, ab-*carboxyethyl-paratolylthiocarbimide*. By interaction with *p*-toluidine; white, glistening, flattened prisms, m. p. $148-149^\circ$.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_{10}H_7$, ab-*carboxyethyl- α -naphthylthiocarbimide*. By interaction with α -naphthylamine; granular prisms, m. p. $183-183.5^\circ$.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_{10}H_7$, ab-*carboxyethyl- β -naphthylthiocarbimide*. Faintly pink plates, having a pearly lustre, m. p. $155-155.5^\circ$.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_3(CH_3)_2$, ab-*carboxyethyl-metoxylthiocarbimide*. By interaction with *m*-xylydine; pearly lozenges, m. p. $152.5-153^\circ$.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_4OH$, ab-*carboxyethyl-*p*-hydroxyphenylthiocarbimide*. By interaction with *p*-amidophenol; oblique rhombic prisms, m. p. $198.5-199^\circ$.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot CH_3$, ab-*carboxyethylmethylthiocarbimide*. By interaction with methylamine; long prisms, m. p. $119-120^\circ$.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_2H_5$, ab-*carboxyethylethylthiocarbimide*. By interaction with ethylamine; fine oblique prisms, m. p. $79-80^\circ$.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_4H_9$, ab-*carboxyethylisobutylthiocarbimide*. By interaction with isobutylamine; feathery tufts of needles, m. p. $53-54^\circ$.

$C_2H_5O \cdot CO \cdot N : C : NH_2 \cdot SH$, *carboxyethylthiourea*. By interaction with ammonia; long prisms, m. p. $139-140^\circ$.

$C_2H_5O \cdot CO \cdot N : C : N : C_6H_5 \cdot C_6H_5 \cdot CH_2 \cdot (SH)$, *carboxyethyl-phenylbenzylthiourea*. By interaction with benzylaniline; long needles, m. p. $93-94^\circ$.

$C_2H_5O \cdot CO \cdot N : C : N : C_5H_{10} \cdot SH$, *carboxyethylpiperidylthiocarbimide*. By interaction with piperidine; fine interlaced needles, m. p. $99-99.5^\circ$.

$C_2H_5O \cdot CO \cdot NH \cdot C \begin{smallmatrix} N \cdot NH \cdot C_6H_5 \\ SH \end{smallmatrix}$, *carboxyethylphenyl-semithiocarbazide*. By interaction with phenylhydrazine; fine white needles, m. p. 146.5° .

The five following esters of thiocarbamic acid were obtained by treating the corresponding alcohols with the thiocarbimide:—

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OCH_3$, *methylic carboxyethylthiocarbamate*. Feathery tufts of needles, m. p. $65-66^\circ$.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OC_2H_5$, *ethylic carboxyethylthiocarbamate* (carboxyethyl- β -thiourethane). Rosettes of faintly yellow needles, m. p. $44-45^\circ$.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OC_3H_7$, *propylic carboxyethylthiocarbamate*. Thick yellow prisms, m. p. $31-32^\circ$.

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OC_4H_9$, *isobutylic carboxyethylthiocarbamate*. A pale greenish yellow liquid, which did not solidify at -8° .

$C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OC_6H_5 \cdot CH_2$, *benzylic carboxyethylthiocarbamate*. Tufts of white needles, m. p. $66-67^\circ$.

In the course of this investigation it is shown that the three following substances, "*ethylic thioaleophanate*" (Peitzsch, *Berichte*, vii., 896), "*ethylic phenylthioaleophanate*," and "*ethylic isophenylthioaleophanate*" (Seidel, *Journ. Prakt. Chem.*, [2], xxxii., 261) have been incorrectly named. The first mentioned appears to be a pseudothiourea; the second an unstable equimolecular combination of ethyl chlorocarbonate and phenylthiocarbamide; whilst the third is identical with the symmetrical carboxyethylphenylthiocarbamide obtained by the writer.

45. "*An Auxiliary Assay Balance.*" By ROBERT LAW, F.I.C.

This paper describes a new form of balance applied to

bullion assaying, the object of which is to give the weight of the gold "cornet" with sufficient accuracy to enable the assayer to put the correct weight in the pan of the ordinary assay balance, and to decide the remaining fractions by means of the rider alone. This auxiliary balance is of such dimensions as to be easily accommodated in the case of the ordinary assay balance. The advantages claimed are—

1. Saving of time in weighing when gold of varying finenesses is under assay.
2. Reduction of the wear in the weights.
3. Increased life for the ordinary assay balance.
4. Avoidance of much of the concentrated attention which tends to make the assayer's work monotonous.

46. "*Charas: the Resin of Indian Hemp.*" By T. B. WOOD, M.A., W. T. N. SPIVEY, M.A., B.Sc., and T. H. EASTERFIELD, M.A., Ph.D.

The authors have examined "*charas*," the exuded resin of *Cannabis indica*, with a view to the isolation of the active principle. The method adopted consisted in the fractional distillation of the ethereal extract prepared from the crude substance. By this means four compounds were isolated:—(1) A terpene, b. p. $170-180^\circ$. (2) A sesquiterpene, b. p. $258-259^\circ$, identical with that previously obtained by Valenta from Personne's "*cannabene*," the green oil obtained when the hemp plant is distilled with water. (3) A paraffin, probably $C_{29}H_{60}$, m. p. $63.5-64^\circ$. (4) A red oil, formula $C_{18}H_{24}O_2$, semi-solid below 60° , and boiling constantly at 265° at 20 m.m. pressure; this compound is present to the extent of 33 per cent in the sample of charas examined. In doses of 0.05 grm. it produces intoxication, followed by sleep. The substance has also been isolated by the authors from a number of pharmaceutical preparations made from the plant. The resin as prepared by T. and H. Smith in 1847 contains no less than 80 per cent of the oil. There can be no doubt that the characteristic action of Indian hemp is due to the presence of this compound, the constitution of which is under investigation.

47. "*Note on the Decomposition of α -Chloronitrocamphor.*" By ARTHUR LAPWORTH, D.Sc.

It has long been known that α -bromo- and α -chloronitrocamphor undergo, when heated, a somewhat violent decomposition, resulting in the liberation of nitrous fumes and free halogen and the formation of products of unknown composition. The author has examined the residual mixtures, and has succeeded in obtaining, by the decomposition of α -chloronitrocamphor, some quantity of a yellow substance, which crystallises in long needles melting at $196-198^\circ$, volatilises slightly at the ordinary temperature, and yields a hydrazone melting at $169-171^\circ$.

This substance proves to be identical with the camphorquinone obtained by Claisen (*Ber.*, xxii., 530) from isonitroso-camphor. Found, C=72.1; H=8.6. Required for $C_{10}H_{14}O_2$, C=72.3; H=8.4 per cent.

48. " *π -Bromocamphor.*" By C. REVIS, Assoc. C.G. Inst., and F. STANLEY KIPPING, Ph.D., D.Sc.

The dextrorotatory π -monobromocamphor which was first obtained by heating camphorsulphonic bromide (Kipping and Pope, *Trans.*, lxxvii., 1895, 371), can be more conveniently prepared from α - π -dibromocamphor (*loc. cit.*). The last-named substance is readily attacked in alcoholic solution by sodium amalgam, and, under suitable conditions, the α -halogen atom only is displaced by hydrogen with formation of π -bromocamphor; the substitution of hydrogen for the α -halogen atom may also be accomplished with the aid of zinc-dust and acetic acid. The yield of the π -bromocamphor is good in both cases, but other products are also formed; the odour of camphor is very noticeable when reduction has proceeded for some time, and a crystalline substance melting at 248° has been isolated in small quantities.

This by-product does not contain bromine, and its formation appears to be the result of condensation, an analysis having given results which point to the formula

$C_{20}H_{30}O_2$. It crystallises in colourless hemimorphic prisms from dilute alcohol, and is readily soluble in chloroform, benzene, and acetic acid.

As π -bromocamphor is now obtainable in large quantities without much difficulty, its derivatives are being investigated. It is easily converted into a crystalline *oxime*, which melts at 124.5° . This oxime crystallises from dilute alcohol in colourless needles, and is readily soluble in chloroform, ethylic acetate, benzene, &c.

The study of the oxime is of particular interest, because if its chemical behaviour should prove to be analogous to that of camphoroxime—as seems to be the case—it will be possible to discuss the structural formulæ for the campholenic acids from a totally new point of view.

49. "Oxidation Products of α -Bromocamphorsulphonic Acid." By ARTHUR LAPWORTH, D.Sc., and F. STANLEY KIPPING, Ph.D., D.Sc.

In the hope of obtaining a new series of oxidation products from camphor, the authors have commenced the examination of the compounds which are formed on boiling moderately concentrated nitric acid with ammonium α -bromocamphorsulphonate.

After heating during many hours, the nitric acid solution contains a small quantity of a substance which is almost insoluble in water, and is deposited in crystals on cooling and diluting. This compound separates from acetic acid in fine orthorhombic prisms. It melts at $188-189^\circ$, and is insoluble in cold dilute sodium carbonate solution; it appears to be a *sulpholactone* derived from a hydroxydibromocamphorsulphonic acid by the elimination of one molecular proportion of water. Found, $C=31.4$, $H=2.96$, $Br=41.3$, $S=8.5$ per cent. $C_7H_{12}SO_4Br_2$ requires $C=30.9$, $H=3.09$; $Br=41.2$, $S=8.2$ per cent.

The acid filtrate from this crystalline substance contains sulphuric acid, but in quantities which show that only a very partial elimination of the sulphonic group has occurred during the oxidation. After removing the sulphuric acid and repeatedly evaporating the filtered solution until almost free from nitric acid, there remains a thick acid syrup, from which it is very difficult to isolate the several constituents; this is owing to the fact that the product consists of hygroscopic sulphonic acids which do not lend themselves to the ordinary processes of extraction, distillation, precipitation, &c.

As the result of a number of operations, however, two crystalline substances have so far been obtained from this mixture. One of these is a sulphonic acid which crystallises from a mixture of methyl alcohol and ethylic acetate in pyramidal forms, and melts at about $156-158^\circ$, with evolution of gas; this compound is very readily soluble in water, from which it separates in hydrated crystals melting at $128-133^\circ$. Analysis of the anhydrous substance gave results agreeing with those required for a *hydroxydibromocamphorsulphonic acid*. (Found, $C=29.9$, $H=3.8$, $Br=38.4$, $S=8.1$ per cent. Calculated for $C_{10}H_{14}SO_5Br_2$, $C=29.5$, $H=3.5$, $Br=39.4$, $S=7.9$ per cent). The other compound isolated from the mixture is apparently the ammonium dihydrogen salt of a π -sulphocamphoric acid. (Found, $C=40.2$, $H=6.4$ per cent. Calculated for $C_{10}H_{15}O_4 \cdot SO_2 \cdot ONH_4$, $C=40.4$, $H=6.4$ per cent), but it requires further analysis; it separates from alcoholic ethyl acetate in microscopic plates, and is extremely soluble in water, but nearly insoluble in cold acetone.

When the crude syrupy oxidation product is freed from water as much as possible, and then treated with phosphorus pentabromide, it yields a considerable proportion of products, which are nearly insoluble in water; from these it is easy to isolate a compound which crystallises from acetone in lustrous prisms, and decomposes at about 191° with effervescence; this substance is insoluble in cold dilute sodium carbonate solution, and only sparingly soluble in most of the ordinary organic solvents; it seems to be a *sulphonic bromide* derived from hydroxydibromocamphorsulphonic acid.

The formation of the dibromo-derivatives described in this note must be partly attributed to the action of the bromine which is liberated during the oxidation of some of the bromocamphorsulphonic acid to sulphocamphoric acid.

50. "On the Xylic and Xylidinic Acids." By WILLIAM HENRY BENTLEY and WILLIAM HENRY PERKIN, jun.

The oxidation of pseudocumene by dilute nitric acid was first carried out by Fittig and Laubinger (*Annalen*, cli., 257), who, by this means, obtained xylic and paraxylic acids, methyl terephthalic acid, and some nitro-compounds.

The authors have found that in addition a small quantity of *methyl isophthalic acid*,—

$CH_3 \cdot C_6H_3(COOH)_2$ [$CH_3 : COOH : COOH = 1 : 2 : 4$], is produced, which is separated from its isomeride by the fractional crystallisation of the methylic salts.

Methylic methylterephthalate crystallises from the methylic alcohol in needles melting at $58-60^\circ$, while methylic methylisophthalate separates in needles melting at 73° .

The reduction products of all four acids are being studied in order to compare their properties with those of some acids obtained from camphoric acid.

Paraxylic acid,—

$(CH_3)_2 \cdot C_6H_3 \cdot COOH$ [$CH_3 : CH_3 : COOH = 1 : 2 : 4$], when reduced with sodium and amyl alcohol yields a mixture of tetra- and hexa-hydroparaxylic acid.

Tetrahydroparaxylic acid, $C_8H_{13} \cdot COOH$, crystallises from light petroleum in prisms melting at 83° , and readily absorbs bromine forming a dibromide, $C_8H_{13}Br_2 \cdot COOH$, which melts at $121-123^\circ$.

Hexahydroparaxylic acid, $C_8H_{15} \cdot COOH$, is an oil with a disagreeable smell, boiling at 251° under a pressure of 748 m.m.

Ethylic hexahydroparaxylate, $C_8H_{15} \cdot COOC_2H_5$, is a pleasant smelling oil boiling at 224° (758 m.m.). The anilide of hexahydroparaxylic acid, $C_8H_{15} \cdot CO \cdot NH \cdot C_6H_5$, separates from light petroleum in prisms melting at $113-115^\circ$.

Hexahydroparaxylic chloride, $C_8H_{15} \cdot CO \cdot Cl$, is a liquid having a disagreeable odour, boiling at 110° (25 m.m.).

Ethylic bromhexahydroparaxylate, $C_8H_{14}Br \cdot COOC_2H_5$, is a heavy liquid, boiling at $170-180^\circ$ (60 m.m.).

PHYSICAL SOCIETY.

Ordinary Meeting, April 24th, 1896.

Captain W. DE W. ABNEY, President, in the Chair.

A PAPER by Mr. R. A. LEHFELDT on "Symbolism in Thermodynamics" was, in the absence of the author, read by the Secretary.

The author proposes a system of about twenty-four separate symbols for the different quantities in thermodynamics.

Prof. SILVANUS THOMPSON said he was not at all favourably impressed by the symbols proposed. In particular, it was becoming usual to restrict the use of Greek letters to the representation of specific quantities or angles, and the author's proposal seemed in this way a retrograde step.

Prof. PERRY said he did not care for the suggested symbols.

Mr. ELDER thought the author's system would be a very severe tax on the memory, for he did not make use of suffixes, which can be made in a great measure to define the symbol to which they are attached.

Mr. APPLEYARD read a paper on "The Adjustment of the Kelvin Bridge."

In a recent paper read before the Society, Mr. Reeves had described a modified form of Kelvin bridge in which a double adjustment was necessary. The author proposes

to employ two wires stretched side by side, with a sliding contact in connection with the galvanometer on each. These contacts are rigidly connected together, so that the segments into which one wire is divided necessarily bear to one another the same ratio as do the segments of the other wire. Hence a single adjustment is sufficient to give balance.

Mr. REEVES said that apparently the author had completely missed the object of his (the speaker's) paper. For the object there aimed at was to make use of such sets of resistance coils as are always to be found in any laboratory. In the author's arrangement it would be necessary to carefully calibrate the two wires, and also, since the resistances used must necessarily be small, to determine the resistance of the contacts.

Prof. AYRTON (communicated) said the author's suggestion was ingenious, but did not obviate the necessity for much of Mr. Reeves's "addition." Further, Mr. Reeves's proposal to employ ordinary resistance boxes was not made because such resistances are absolutely necessary, but because since they are to be found in every laboratory, their use saves the expense of such a wire resistance, accurately calibrated, as Mr. Appleyard employed.

Mr. APPLEYARD, in his reply, said that his instrument was designed for use in a factory, where the time saved in making a series of tests was of more importance than the cost of the instrument.

Mr. J. FRITH read a paper on "*The Effect of Wave-Form on the Alternate Current Arc.*"

The author finds that an arc has the power of modifying the wave-form in a circuit in which it is included. Thus, in the case of a dynamo for which, on open circuit, the curve of E.M.F. was decidedly peaked, it was found that when this dynamo was employed to feed an arc that the curve became changed to a flat-topped form. It is interesting to remember that the candle-power of the arc is greater when the wave-form is flat-topped than when it is peaked. By altering the resistance in series with the arc, it is possible to alter the character of the curve; for, as the resistance in series with the arc increases, the arc affects the wave-form less and less. In some recent experiments described by Dr. Fleming, a resistance of about 7 ohms was used in series with the arc, so that the wave-form of the generator, which is not an efficient form, was forced on the arc. In practice, however, where a resistance is not used in series with the arc this is not the case, and the differences between the efficiency obtained for alternate current arcs in the laboratory and that claimed in practice may thus be accounted for.

Mr. BLAKESLEY said it seemed as if the more nearly the alternate current resembles a direct current, and the longer in each period the current remains constant, the greater is the efficiency of the arc.

Mr. PRICE asked what was the cause of the reaction of the arc on the wave-form?

Mr. TREMLETT CARTER asked whether previous observers' results were vitiated by this action of the arc on the wave form?

Prof. AYRTON (communicated) considered the author's suggestion of great importance, as bearing on the efficiency of the alternate current arc.

Prof. S. P. THOMPSON said that the dynamo employed by the author was one in which there was a large quantity of iron in the armature, so that the self-induction was large. Was it not on account of this large coefficient of self-induction, which would tend to keep the current constant, that the arc was able to alter the wave-curve? If an arc is connected to the mains of a supply station in which a number of machines in parallel are feeding a number of lamps, would the arc still be able to affect the wave-form of the current?

Mr. TREMLETT CARTER asked if the author had tried the effect of replacing the arc by a resistance such that it would absorb the same volts as did the arc, and comparing

the curves for the current and impressed P.D. with those obtained with the arc.

The AUTHOR, in his reply, said that the effect of the self-induction of the machine was shown in the curves. Current curves had not been taken with the arc straight on the machine. The current and self-induction were the same for all the curves, the voltage of the machine being increased by increasing the field when resistance was placed in series with the arc. When, as is commonly the case, special machines are used to supply arcs, and the load consists solely of arcs, the arcs could alter the character of the wave form. If the arc is replaced by a resistance, the wave form is of the same type as is obtained for the E.M.F. of the machine on open circuit.

The Society then adjourned till May 8th.

NOTICES OF BOOKS.

Chemical Novelties, New Laboratory Appliances, New Methods of Researches applied to Science and to Industry. ("Les Nouveautés Chimiques, Nouveaux Appareils de Laboratoire, Méthodes Nouvelles de Recherches appliquées à la Science et à l'Industrie.") By CAMILLE POULENC, D.Sc. Paris: J. B. Baillière and Son; Poulenc Frères. 8vo., pp. 136.

THIS profusely illustrated work is devoted to the description of new and improved laboratory apparatus. Among these may be especially mentioned Mercier's new ureometer, Bernard's calcimeter, Moissan's apparatus for the determination of boron, Bourlier's arrangement for the determination of plaster in wine, Nevière and Hubert's instrument for the recognition of fluorine in wines, and Procter's tintometer and colorimeter—a modification of the well-known instrument of Lovibond. There is also a description and figure of M. Tniery's comparative hemaspéctroscope, by means of which it is said that 1 part of blood may be detected in 850,000 parts of any liquid.

There is also an account of Schlumberger's "aseptic filter," which is said to effect a perfect sterilisation not merely of ordinary river waters, but even of sewage. The ordinary filtering materials are coated with aluminium benzoate and manganic carbon.

Fruit and Gardens for the People. By the Hon. DUDLEY CAMPBELL. A Preface to the "Case against Butchers' Meat," by CHARLES W. FORWARD. London: Bennett and Russell, Ltd. 1896.

THIS pamphlet, as appears from its second title, is a vegetarian manifesto, and as such lies distinctly outside the jurisdiction of the CHEMICAL NEWS.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 13, March 30, 1896.

Different Properties of the Invisible Radiations emitted by the Salts of Uranium, and of the Radiation of the Antikathodic Wall of a Crookes Tube.—Henri Becquerel.—Inserted in full.

Penetration of Gases into the Glass Walls of Crookes Tubes.—M. Gouy.—Already inserted.

Use of Heteroform Magnetic Fields in Photography by the X Rays.—Georges Meslin.—Already inserted.

Time of Exposure in Photographs by the X Rays.—James Chappuis.—Will be inserted in full.

Action of the X Rays upon Electrified Bodies.—L. Benoist and D. Hurmuzescu.—Will be inserted in full.

Refraction of Röntgen's Rays.—F. Beauland.

Diffraction and Polarisation of Röntgen's Rays.—G. Sagnac.—(See p. 201).

Stereoscopic Photographs obtained with the X Rays.—A. Imbert and H. Bertin-Sans.—The authors describe the arrangement which they have employed for surgical purposes in detecting the position of a foreign body within human tissues.

Determination of the Depth or the Position of a Foreign Body in the Tissues by means of the X Rays.—Abel Buguet and Albert Gascard.—Further surgical applications of the Röntgen rays.

Action of the X Rays upon a Phycomyces.—L. Errera.—It appears from the author's experiments, conducted at the Solvay Institute of the University of Brussels, that the phycomyces is not sensitive to the Röntgen rays.

On the Röntgen Rays.—Charles Henry.—This paper will be inserted as early as possible.

Reply to some Observations of Henri Becquerel on a Paper "On the Principle of an Accumulator of Light."—Charles Henry.

Observations relating to Charles Henry's Reply.—Henri Becquerel.

Safrol and Isosafrol. Synthesis of Isosafrol.—Ch. Moreu.—The synthesis of isosafrol, setting out from methylene-homocafeic acid, establishes its constitution in an indisputable manner; it shows that this compound is certainly propenylmethylene-pyrocatechine. If we proceed by the method of exclusion safrol will be allylmethylene-pyrocatechine.

On Citronnellol and its Isomery with Rhodinol.—Ph. Barbier and L. Bouveault.—Rhodinol is distinct from citronnellol since the corresponding acids are distinct.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. x., Nos. 119 and 120.

These issues contain no chemical matter.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Society of Arts, 8. (Cantor Lectures). "Applied Electro-Chemistry," by James Swirburne.

— Society of Chemical Industry, 8. "Reproduction of Colour by Photography," by E. J. Wall. "Artificial Silk," by Messrs. Cross and Bevan.

TUESDAY, 5th.—Royal Institution, 3. "Ripples in Air and on Water," by C. V. Boys, F.R.S.

— Society of Arts, 8. "Australia's Prospects in British Markets," by James F. Dowling.

— Institute of Civil Engineers, 8.

— Pathological, 8.30.

WEDNESDAY, 6th.—Society of Arts, 8. "High Explosives and Smokeless Powders," by Hudson Maxim.

— Society of Public Analysts, 8. "The Composition of Human Fat," by C. A. Mitchell, B.A.

— "Note on an Incrustation found in Hot-water Pipes," by J. Augustus Voelcker, M.A., B.Sc., Ph.D. "The Examination of Commercial Milk Sugar," by H. Droop Richmond. "Note on 'Drawn' or Exhausted Caraways," by Bernard Dyer, D.Sc., and J. F. H. Gilbard.

THURSDAY, 7th.—Royal, 4.30.

— Royal Institution, 3. "The Art of Working Metals in Japan," by W. Gowland, F.C.S.

— Chemical, 8. "Ballot for Election of Fellows.

FRIDAY, 8th.—Royal Institution, 9. Electric Shadows and Luminescence," by Prof. Silvanus P. Thompson, F.R.S.

— Astronomical, 8.

— Physical, 5.

SATURDAY, 2nd.—Royal Institution, 3. "Three Emotional Composers—I. Berlioz," by F. Corder, Curator, Royal Academy of Music.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1902.

ON THE MECHANICAL ACTION EMANATING FROM CROOKES TUBES.

By A. FONTANA and A. UMANI.

In the *Comptes Rendus* for March 23rd there was published a paper by J. R. Rydberg "On Mechanical Action emanating from Crookes Tubes." We must make known that we have developed this subject in a memoir published in the *Rendiconti della R. Accademia dei Lincei* (vol. v., March 1, 1896), entitled "Azione del Tubo di Crookes sul Radiometro."

We have observed the facts described by Gossart and Chevalier (*Comptes Rendus*, Feb. 10, 1896), but, contrary to the conclusions of these authors, we have found that the mechanical action is due to charges of statical electricity, and not to the rays of Röntgen.

We have reproduced these facts without the intervention of a Crookes tube, with the aid of a Leyden jar. On the other hand, we have pointed out that the mechanical action upon the wings fades away when we shut up the Crookes tube, and the coil or the radiometer, in a metallic chest placed in communication with the earth.

We have also studied the action of various diaphragms, and observed that the permeability, greater or smaller for the X rays, has no influence on the directive force of the tube, and, on the contrary, that diaphragms which are good conductors of electricity in connection arrest the mechanical action, whilst dielectrics do not arrest it.

We believe, therefore, that we have been the first to exclude all relation between the rays of Röntgen and the phenomena observed with the Crookes tube, and to deny the accuracy of the method proposed for measuring the intensity of the X rays.—*Comptes Rendus*, cxxii., p. 840.

APPLICATION OF PHOTOGRAPHY BY RÖNTGEN RAYS TO ANALYTICAL RESEARCHES ON VEGETABLE MATTER.

By FERNAND RANVEZ.

PHOTOGRAPHY by means of the X rays can render precious services in analytical research, and especially in the analysis of vegetable articles of food, where it will detect certain of the most frequent falsifications—those effected by the addition of mineral substances.

This method offers manifold advantages: it requires only small quantities of the substances; it leaves the specimens completely intact; it allows us to effect in a very short time a great number of examinations (about a quarter of an hour sufficing for a series of specimens). Lastly, the proof obtained is a piece of convictive evidence quite demonstrative, easily understood even by persons strange to any analytical operation.

The experiments which I have made refer to three samples of falsified saffron, taken in trade. These products consisted of mixtures in different proportions of pure saffron and saffron coated with barium sulphate. The filaments of the latter were found surrounded with a shell of mineral matter. The adulteration was very skilfully masked, and could not be suspected on a mere inspection of the merchandise.

I arranged on one and the same sensitive plate, enclosed in black paper, quantities of the three adulterated samples

almost equal. No. II. contains 62.13 per cent of mineral matters, No. III. 28.69 per cent, No. IV. 22.21 per cent, and along with them a specimen of pure saffron. The whole was submitted for three minutes to the influence of the rays emanating from a Crookes tube.

The pure allowed itself to be traversed by the X rays, and produced on the proof merely shadows scarcely visible, not acting, so to say, upon the paper of the positive proofs. The three falsified samples acted strongly upon the sensitive plate, marking very distinctly the filaments coated with barium sulphate, whilst the stigmata of the pure product, which were mixed with it, appeared only as scarcely perceptible shadows analogous to those of the former product.

The photographic proofs which accompany this note show the distinctness of the results obtained, and enable us to foresee the services which this method will render in its future applications.—*Comptes Rendus*, cxxii., p. 841.

ACTION OF THE X RAYS UPON ELECTRISED BODIES.

By L. BENOIST and D. HURMUZESCU.

SINCE our first communication on the X rays (February 3), in which we announced that these rays have the property of completely discharging electrised bodies without causing new electrification to appear, and in which we founded upon this property an actinometric method applicable to these radiations, there have been published several memoirs relating to the same phenomena. That of J. J. Thomson formulates conclusions entirely in agreement with our own. The others, such as that of A. Righi, that of Borgmann and Gerchun, and that of H. Dufour, whilst agreeing as concerns the discharge of electrised bodies, whatever is the sign of their electrification, signalise an electrification produced directly by these rays without agreeing as to the sign of this electrification, which is positive according to Righi, but negative according to Borgmann and Gerchun.

In view of these discrepancies, we thought it well to repeat our former experiments, greatly prolonging the action of the Crookes tube upon the gold leaves of the electroscope. We constantly observed a complete collapse, whatever was the sign of the original charge, and the complete absence of any new ultimate divergence.

Fearing a default of sensitiveness for weak charges in the electroscope, we employed a new type of symmetrical mirror electrometer* always completely enclosed in a metal cage communicating with the earth. In the interior of this cage is found, behind a window closed with a leaf of aluminium, the proof-plate which, at the outset of each experiment, is charged to a potential of about 60 volts. The dielectric which insulates the electrised bodies is absolutely protected from any action on the part of the Crookes tube.

Under these conditions, the discharge was again absolutely complete and definite, whatever was the sign of the initial charge, and whatever the nature of the metal forming the proof-plate. For we asked ourselves whether the discrepancies above mentioned might not arise from the nature of the metal. Then, if the X rays can develop an electric charge, of which we have not yet been able to observe any trace, this effect does not exceed the order of magnitude of the electrometer forces of contact.

But in the course of these new experiments, we have discovered a new specific property of different bodies, and particularly of metals in reference to the X rays. The metals being taken in discs of the same diameter, and the influence of the variations of the Crookes tube having been ascertained by the method of alternate means, we

* See "Les Rayons X et la Photographie à travers les corps opaques," Ch. Ed. Guillaume, p. 89, Fig. 16.

have observed that the time of fall from a given potential to another varies with the nature of the metal exposed. This is also the character presented by the loss of electricity under the action of the ultra-violet rays.

But the order of the different metals is not the same in both cases. It is known that, according to Leonard and Wolf, who explain these phenomena by a pulverisation of the metal, silver is the most sensitive to discharge by the ultra-violet rays; then follow gold, iron, lead, tin, copper, platinum, mercury, and zinc. But silver and zinc, which occupy the two extremities of this list, are, on the contrary, very near each other in the list which we have obtained as regards the action of the X rays, and they occupy the middle, along with gold, iron, nickel, zinc, brass, and copper. At the extremities we find, on the one hand, aluminium, in which loss is very slow; and on the other platinum and mercury, in which it is very rapid.

Here follow some figures showing the duration of one and the same fall of potential, taking as unity that of platinum:—

Zinc and brass amalgamated	0.96
Platinum, in thin plates	1.0
„ in beaten leaves	1.1
Ferro-nickel	1.38
Zinc	1.41
Silver, in beaten leaves	1.48
Red copper	1.53
Silver, in plates	1.92
Aluminium, hammered	2.12
„ in plates	1.97
Lamp-black	1.97

These figures are evidently in relation with the tube which we have employed, in view of the heterogeneity of the X rays which we have already demonstrated.

Hence the aptitude of the different metals to utilise the energy of the X rays for dissipating electricity distinctly varies inversely as their transparency for these rays, since aluminium is decidedly the most transparent of the above metals, whilst platinum and mercury are the most opaque. This aptitude represents a sort of absorbing power, comparable to that of bodies more or less opaque to the luminous and thermic radiations.

Further, this absorbent power has its seat in the superficial layer of the metal itself, as it increases distinctly with the thickness of this metal when such thickness is still very trifling.

Lamp-black, transparent to the X rays, is precisely as little absorbent for aluminium. Thus, the time of discharge for a plate of polished copper varies from 1.52 to 1.97 when it is coated with lamp-black.

Without, as yet, giving a complete explanation of these phenomena, in view of which we have prepared various experiments, we believe that we may present the following observations:—

1. The theory of pulverisation does not give this explanation, since it does not appear compatible with the fact observed by us, and also by J. J. Thomson, that the discharge of the electrified metals is effected completely, not only in the air, but also in a solid dielectric medium, like paraffin.

2. The property which dielectrics possess of becoming conductors under the action of the X rays—a property formulated by J. J. Thomson—does not suffice to explain all the circumstances of the phenomena, since the nature of the metal distinctly intervenes up to a certain depth. We have further observed that the relation of the times of discharge found for two different metal surfaces is not modified when the two surfaces are entirely covered with a layer of paraffin of the same thickness. We arranged to repeat this experiment, changing the nature of the dielectric covering.

The results which we have just stated seem to us to indicate in what direction future researches must be conducted in order to obtain preparations more sensitive to the X rays in photography than plates of silver gelatino-

bromide. The salts of platinum, being more absorbent, will doubtless be more advantageous, which we purpose to verify.—*Comptes Rendus*, cxxii., p. 779.

ON THE DIFFRACTION OF THE RÖNTGEN RAYS.

By L. CALMETTE and G. T. HUILLIER.

WE have the honour of submitting to the Academy some photographic proofs obtained with the Röntgen rays by means of the following arrangement:—

Very near the Crookes tube there is a screen E of brass perforated by a slit, the width of which has rarely reached a half m.m. A second metal screen, E', is formed of a plate provided with two slits or pierced with a window in which is fixed a metal rod of 1 m.m. in diameter. This screen is placed at the distance *a* behind the former. Lastly, a photographic plate, enfolded in two leaves of black paper, is placed at the distance *b* behind the second screen E'.

The following table indicates, for each proof, what is the screen E' used, and the value of *a* and *b+a*:—

No.	E'.	<i>a</i> . Cm.	<i>b+a</i> . Cm.
1.	Rod of 1 m.m. in diameter..	5	19.5
3.	„ „ „ „	5.5	20
5.	„ „ „ „	8.9	30
7.	Two narrow slits, separated by a cylindrical rod of 1 m.m. in diameter	?	?

On the proofs 1, 3, 5 the shadow thrown by the metallic rod is bordered on each side by a light band which shows a maximum of intensity. Within this shade we observe a zone less dark, which seems to indicate that the Röntgen rays penetrate into the geometrical shadow. Lastly, in proofs 3 and 5 we see, in like manner, a maximum of intensity along the margins of the window in which the rod is placed.

In the proof No. 7 we perceive, in the middle of the two white bands, a fine dark ray, whilst in the shadow of the rod which separates the two slits there is seen a light ray.

If we compare these results with those obtained with light in the same conditions, the slit being relatively wide and the intensity weak, it seems difficult not to ascribe them to the diffraction of the Röntgen rays.

The proofs obtained in these experiments—which we propose to continue—are not yet so distinct that we can measure the wave-length with any precision. But we are still led to believe that this wave-length is greater than that of the luminous rays.—*Comptes Rendus*, cxxii., p. 877.

VOLUMETRIC DETERMINATION OF THE PHOSPHORIC ACID SOLUBLE IN WATER EXISTING IN SUPERPHOSPHATES.

By C. GLASER.

THE author's process is founded on the methods of Emmerling, Kalmann, and of Meissels. The chief condition for obtaining accurate results is the addition of an excess of perfectly neutral calcium chloride, after it has been adjusted to neutrality with methyl-orange. The presence of iron and aluminium salts in large quantities has a disturbing effect, as also certain organic substances which may render the result too high. For a determination the author proceeds as follows:—

Two grms. superphosphate are repeatedly stirred up with much water, and after repeated decantation washed on the filter until 250 c.c. of filtrate are obtained: 50 c.c.

of the filtrate, after the addition of 2 drops of methyl-orange solution, are titrated with decinormal soda until the acid reaction has *completely* disappeared. This point is not quite easy to reach. We then add neutral solution of calcium chloride, whereon, in presence of iron and aluminium, there occurs a slight return to an acid reaction, which does not need to be regarded. We next add 5 drops of solution of phenolphthalein, and titrate with decinormal alkali until an alkaline reaction is just perceptible throughout the entire liquid. This is the correct terminal point. The alkaline reaction soon disappears again, and several more c.c. of alkali may be added until it becomes permanent; but the quantity is thus exceeded. It is advisable, in order to obtain quite sharp results, to put the liquid in quick rotation in a tall beaker, and to keep up this movement until the alkaline reaction makes its first appearance. We then read off quickly, and satisfy ourselves, by the addition of a few more c.c. of alkali, that we are not mistaken as to the final point.

On dull days it is recommended to view the liquid by concentrated light (a full, large washing-bottle).

Each c.c. of soda-lye corresponds in the first part of the titration (methyl-orange) to 7.1 m.grms. tartaric acid, and in the second (phenolphthalein) to 3.55 m.grms. If larger quantities are used, as proposed by Kalmann and Meissels, the use of semi-normal soda may be preferable. The changes of colour are then strong and more distinct. In twenty samples of superphosphate the mean result, by the above method, was 21.345 per cent soluble phosphoric acid, as against 21.256 found gravimetrically.

The attempt was made to determine the total phosphoric acid volumetrically, after previous adjustment with methyl-orange. The mean obtained was 16.65 (gravimetrically 15.50), but in some cases the discrepancies were too great, and the final reaction could not always be recognised with the distinctness desirable.—*Chemiker Zeitung* and *Zeit. Anal. Chemie*, xxxiv., p. 768).

ON COLOUR PHOTOGRAPHY BY THE INTERFERENTIAL METHOD.*

By G. LIPPMANN,
Professor of Physics, Faculty of Sciences, Paris.

COLOUR photographs of the spectrum, or of any other object, are obtained by the following method:—A *transparent* photographic film of any kind has to be placed in contact with a metallic *mirror* during exposure. It is then developed and fixed by the usual means employed in photography, the result being a *fixed* colour photograph visible by reflected light.

The mirror is easily formed by means of mercury. The glass plate carrying the film being inclosed in a camera slide, a quantum of mercury is allowed to flow in from a small reservoir and fill the back part of the slide, which is made mercury-tight. The plate is turned with its glass side towards the objective, the sensitised film touching the layer of mercury. After exposition, the mercury is allowed to flow back into its reservoir, and the plate taken out for development.

The only two conditions necessary for obtaining colour, transparency of the film, and the presence of a mirror during development, are physical conditions. The chemical nature of the photographic layer has only secondary importance; any substance capable of giving, by means of an appropriate development, a fixed colourless photograph is found to give, when backed by the mirror, a fixed colour photograph.

We may take, for instance, as a sensitive film, a layer of albumen-iodide of silver, with an acid developer; or a layer of gelatino-bromide of silver, with pyrogallie acid, or with amidol, as developers. Cyanide or bromide of

potassium may be as usual employed for fixing the image. In a word, the technics of ordinary photography remain unchanged. Even the secondary processes of intensification and of isochromatisation are employed with full success for colour photography.

The photographic films commonly in use are found to be opaque, and formed, in fact, by grains of light-sensitive matter mechanically imprisoned by a substratum of gelatin, albumen, and collodion. What is here wanted is a fully transparent film, the light-sensitive matter pervading the whole of the neutral substratum. How can such a transparent film be realised? This question remained insoluble to me for many years, so that I was debarred trying the above method when I first thought of it. The difficulty, however, is simply solved by the following remark. It is well known that the precipitation of a metallic compound, such as bromide of silver, does not take place in the presence of an organic colloid, such as albumen, gelatin, or collodion. In reality, the metallic compound is formed, but remains invisible; it is retained in a transparent modification by the organic substances. We have only, therefore, to prepare the films in the usual way, but with a stronger proportion of the organic substratum; the result is a transparent film. By mixing, for instance, a gelatinous solution of nitrate of silver with a gelatinous solution of bromide of potassium, no precipitate is formed, and the result is a transparent film of dry gelatin containing 15 and even 30 per cent of the weight of bromide of silver.

The colours reflected by the film are due to interference: they are of the same kind as those reflected by soap bubbles or by Newton's rings. When a ray of definite wave-length falls on the sensitive plate, it is during exposition reflected back by the mirror, and then gives rise to a set of standing waves in the interior of the film, the distance between two successive loops being equal to half the wave-length of the luminous ray. This system of standing waves impresses its periodical structure on the film. The photographic deposit, therefore, takes the form of a grating, a continuous grating, perfectly adapted for reflecting the particular luminous ray which has given it birth.

This theory can be subjected to experimental proof. If we examine a photograph of the spectrum, or any other object by white light, we observe the following facts:—1. Colours are seen in the direction of specular reflection, and are invisible in every other direction. 2. The colours change with the incidence; the red changing successively to green, blue, and violet, when the incidence grows more oblique. The whole image of the spectrum is displaced, and gradually passes into the infra-red region. 3. If the film be gradually imbibed with moisture, the colour changes in the opposite direction, from red to violet. This phenomenon is due to the swelling up of the gelatin albumen, causing the intervals between the elements of the grating to become larger. The smaller intervals, corresponding to violet and blue light, gradually swell up to the values proper to red and infra-red waves. A photograph immersed in water loses all its colours, these appearing again during the process of drying. For the same reason, a freshly-prepared plate has to be dried before the correct colours can be finally seen.

We have now to consider the case of compound colours, and to generalise the former theory, which is only applicable to the action of simple rays. I beg to subjoin an abstract of this generalised theory. It will be seen that if a compound ray of definite composition impresses the plate, it gives rise during exposure to a definite set of standing waves, which impress their structure on the film, and impart to the photographic deposit a corresponding definite form. Though very complex, this can be described as made up of a number of elementary gratings, each corresponding to one of the simple rays which contribute the impressing light. When examined by white light, the reflected ray is shown to have the same composition as the impressing ray; white light, for instance, imparts

* A Paper read before the Royal Society, April 23, 1896.

to the photographic deposit such a structure that it is adapted to reflect white light.

The only *à priori* condition for the correct rendering of compound rays, is a correct isochromatisation of the film. This, again, can be practically effected by known processes, such as have been indicated by E. Becquerel, Vogel, Captain Abney, and others.

As a verification of this theory, I beg leave to project on the screen a series of colour photographs, representing natural objects: pictures on stained glass, landscapes from nature, flowers, and a portrait from life. Every colour in nature, including white, and the delicate hue of the human complexion, is thus shown to be reflected by a correctly developed photographic film.

It is to be remarked that, as in the case of the spectrum, the colours are visible only in the direction of specular reflection. If I had tried to touch up these photographs by means of water colours or other pigments, these would be made apparent by slightly turning the photograph; these pigments remaining visible under every incidence, they would thus be seen to stand out on a colourless background. Thus the touching up or falsifying by hand of a colour photograph is happily made impossible.

BERTHELOT'S CONTRIBUTIONS TO THE HISTORY OF CHEMISTRY.*

By H. CARRINGTON BOLTON, Ph.D.

MARCELLIN BERTHELOT, Professor of Chemistry in the Collège de France, Perpetual Secretary of the Academy of Sciences, Senator, Minister of Public Instruction, and recently appointed Minister of Foreign Affairs, known to the scientific world by his masterly researches in synthetic chemistry, has added to these honours that of editing the most important and far-reaching documents pertaining to the history of chemistry ever brought to light.

The six handsome quarto volumes published by him between the years 1887 and 1893 contain the most ancient Greek, Arabic, Syriac, and Latin treatises on alchemy and technical chemistry preserved in the great libraries of the Old World. Besides reproducing the original text of these precious manuscripts, these volumes contain complete translations of many treatises, analyses of the contents of others, and critical studies of their mutual relations, their sources and authorship, as well as erudite essays on the chemical knowledge exhibited in them. The six volumes form two distinct works: three of the volumes bear the title "*Collection des anciens Alchimistes Grecs*," and three of them "*La Chimie au moyen âge*," each volume having, moreover, specific sub-titles more exactly indicating its contents.

Not having seen any adequate review of these works in English, I propose in this article to examine their scope, contents, and manner of treatment, as well as to show some of the more important changes resulting from Berthelot's historical studies. The existence of ancient Greek and Arabian manuscripts had long been known; Reuvens, and later Leemans, of Holland, had published summaries of certain papyri preserved in Leyden, more than forty years before, but in such a fragmentary manner as merely to excite curiosity. Ferdinand Hoefer, the French historian of chemistry, and Herman Kopp, the erudite German, had made partial use of some of the manuscripts; but it remained for Berthelot to collect and compare the diverse copies, to reproduce and translate them for the benefit of students. This he could scarcely have accomplished without the aid of the French Government, both series being "published under the auspices of the Minister of Public Instruction." Government co-

operation was brought about through a report made by Berthelot to the "*Comité des Travaux Historiques et Scientifiques*," and adopted by them in 1884. This report directed attention to the existence of Greek alchemical manuscripts and to the utility of their publication, owing to the great light they throw on the history of natural science, the technology of metals and ceramics, and the history of philosophy in the first centuries of the Christian era.

The difficulties of deciphering, transcribing, and editing Greek, Arabic, Syriac, and Latin manuscripts were prodigious, and Berthelot was fortunate in securing scholars of eminence to assist in the task. In dealing with the Greek papyri, he was aided by Ch. Em. Ruelle, of the Bibliothèque Sainte Geneviève, Paris, and by André Berthelot, son of the editor; the Arabic scholar, Professor Houdas, and the Syriac linguist, Rubens Duval, also contributed their learning, each in his own sphere.

The "*Collection des Alchimistes Grecs*" opens with an "Introduction" by Berthelot, which occupies 268 pages; this forms an important contribution to the history of chemistry, based upon a critical study of the ancient treatises; he agrees with other historians in tracing the birth of alchemical ideas to Egyptians, whence they reached Europe through Greeks.

Certain Greco-Egyptian papyri, preserved in Leyden, are of the greatest interest; several of them treat of magical formulas, incantations, love philtres, dreams, and similar gnostic notions; one of them, known as "*Papyrus X*," is a treasury of information on metallurgical operations, at so early a period as the third century of the Christian era. It was found in a tomb at Thebes, secured by the Swedish Consul at Alexandria, Anastasi, and presented by him to the Netherlands in 1828. Berthelot conjectures it is one of the ancient Egyptian books on the preparation of gold and silver, which escaped the destruction ordered by Diocletian in 290,—an order issued lest the people using them should grow rich by their art and revolt against the Romans.

This precious document contains one hundred and one chemical and alchemical recipes, followed by ten paragraphs taken from Dioscorides. The recipes are for making alloys to be used in the manufacture of cups, vases, images, and other objects of the goldsmith's art, also processes for soldering metals and superficially colouring them, besides formulas for making gold and silver inks. The text is full of grammatical errors and ignorant spellings, which show the writing to have been the work of an uneducated artisan; the recipes are not arranged in order, several appear in duplicate,—they exhibit no indication of chicanery, although some of the methods are unprofitable. The whole papyrus, in short, is evidently the memorandum-book of a goldsmith (or silversmith) engaged in attempts to imitate gold and silver for fraudulent purposes. Only one author is cited, "*Phimenas*," who is probably Pammenes, author of recipes occurring also in other manuscripts. The preparation of *asen*, an amalgam of copper and tin, plays a prominent part among the recipes for imitating gold. But time forbids a full analysis of this remarkable manuscript; as a result of Berthelot's careful study of this and analogous treatises, he comes to the conclusion that the doctrines of alchemy concerning the transmutation of metals did not originate in the philosophical views of the constitution of matter, as generally supposed, but in the practical experiments of goldsmiths occupied in making fraudulent substitutes for the precious metals. The "Introduction" contains a chapter on the relations between the metals and the planets, of Chaldean origin, and constant occurrence in the early writings, which is illustrated by facsimiles of several manuscript pages. Another chapter is devoted to the figures of apparatus occurring in the treatises of the eleventh to fourteenth centuries; these include water-baths, digestors, aludels, alembics, and a great variety of apparatus for distillation.

* Read before the Washington Section of the American Chemical Society, March 12, 1896. Advance Proofs from *Journal of the American Chemical Society*.

The sixth chapter of the Introduction is divided into twelve sections; these deal with several Greek manuscripts, notably those preserved in the libraries of St. Mark, Venice, the Escorial, the Vatican, Rome, Gotha, and in Munich, appertaining to the eleventh to fourteenth centuries; of these we note only a few features. At the beginning of the MS. of St. Mark, in one of the earliest of chemical bibliographies, it gives the title of fifty-two treatises, verily not in modern style, yet quite suggestive; among them are the following:—"Emperor Heraclius, eleven chapters on the manufacture of gold." "Justinian, five chapters on the secret art." "Heliodorus, on the divine art." "Theophrastus, verses on this art." "Moses, on the diplois (doubling) of gold." "Lexicon of the gold-maker, in alphabetical order."

This association of names of Emperors of Rome, Greek classical writers, and the Hebrew lawgiver, with chemical and alchemical treatises, is characteristic of the period at which they were compiled, and by no means denotes actual authorship; the names of prominent men were given to the treatises in order to add to the dignity and authority of the writings. This custom prevailed as late as the sixteenth century, and, in certain cases to be noted hereafter, gave rise to undeserved honours. An entire group of writings have been ascribed to Democritus, giving rise in Egypt to what may be styled the school of Democritus. A certain Zosimus, of Panopolis, is credited with a veritable encyclopædia of the sacred art, a work which occupies ninety pages of Berthelot's volume.

The Collection des Alchimistes Grecs comprises no less than 160 different treatises on the science of Hermes. Many of these are fragmentary in the extreme, extending to only six lines, and even less. All are composed in an archaic, enigmatical style, combining, in one undecipherable medley, chemical terms of obscure meaning, magical formulas, astrological notions, citations from mythical authors, and mystical allusions to a philosophy long since buried too deep for present resurrection. It is not surprising that commentators early felt the need of lexicons of the sacred art, and such are preserved in these volumes; unfortunately, however, the definitions are no clearer than the words defined; one word was often used for a score of different objects and processes, and a single article was known by a dozen different names. To convey to readers any idea of these extraordinary literary productions by citations is hardly practicable in the space available, for passages lose much when removed from their original settings. The actual chemical knowledge exhibited in these ancient manuscripts is varied, and yet indefinite owing to the numerous obscure expressions; the authors were acquainted with a large number of ores, minerals, earthy substances, and saline bodies, as well as vegetable and animal products, but their ignorance of the mineral acids and their important derivatives limited them to products obtained by aqueous solution, distillation, and the action of heat. Of scientifically classified knowledge there is no trace; the alleged opinions of mythical writers are given as authoritative, and information is imparted in the tedious form of dialogues between philosophers, who remind one of the Scotchman's definition of metaphysicians—"Poor bodies discussing things of which they know nothing in a language neither of them can understand." Many of the writings contain reverent acknowledgments of the Deity and other evidences of piety. There is a good deal of duplication, arising from the introduction into an essay of passages from another, generally without acknowledgment.

Berthelot remarks incidentally that the term *Philosophers' Stone* does not occur in writings earlier than the seventh century, although the central idea is much more ancient.

Each of the three quarto volumes which constitute Berthelot's "*La Chimie au moyen âge*" bears an independent title; that of the first volume reads—"Essay on the transmission of the knowledge of Antiquity to the Middle Ages; transmission of Technology; translations

of Arabico-Latin treatises, with a new version of the *Liber Ignium* of Marcus Græcus, and an original edition of the *Liber Sacerdotum*."

This volume covers the period from the fall of the Roman Empire to the thirteenth century, thus filling the gap between the ancient Greek alchemists and the Latin writers of the later epoch, a period which had been previously unworked or misunderstood. Berthelot finds that the transmission from the earlier to the later era was accomplished by two agencies; first through the Arabians, who succeeded to the literary and scientific wealth of the Greeks. The Arabic treatises, preserved in the Mohammedan libraries of Spain, were translated into Latin, and thus became for Western nations the sources of their knowledge in medicine, alchemy, mathematics, and philosophy. Some of these translations were collected and printed in the seventeenth century in the works entitled *Theatrum Chemicum* (5 vols., 1613-22), and *Bibliotheca Chemica*, of Mangetus (2 vols., folio, 1702), and Berthelot discovered in these Arabico-Latin treatises entire passages from the ancient Greek Alchemists.

The connection between the Greeks and Arabians was not, however, immediate, but through the Syrians, who were among the first to translate the philosophy and science of the Greeks into an oriental tongue. These Syriac versions form the subject of the second volume.

A second link between the Greeks and the Latin alchemy was more directly forged, though difficult of recognition; the processes used in industrial arts and metallurgical operations by the Greeks had been adopted by the Latins as early as the time of the Roman Empire, and this chemical technology was preserved through centuries of intellectual degradation to the beginning of the Middle Ages.

The most ancient Latin treatises on chemical technology are the *Compositiones ad tingenda*, dating from the close of the eighth century, and the *Mappæ clavicula*, written before the tenth century. These are collections of recipes for industrial processes analogous to those in the Leyden papyrus, and forming links in a chain that extends from that ancient work through the treatises of the Middle Ages to the modern "Workshop Recipes" and "Manuels Rorets." The full title of the *Compositiones ad tingenda* is as follows: [Translation.]—"Recipes for colouring mosaics, skins, and other objects, for gilding iron, for using minerals, for writing in letters of gold, for soldering metals, and other technical documents." The following are some of the subjects treated:—The colouring of artificial stones, used in the manufacture of mosaics; the manufacture of stained glass; the dyeing of skins in purple, green, yellow, and reds; the dyeing of wood, bone, and horn; a list of ores, metals, earths, and metallic oxides, used in jewellery and in painting; a number of recipes for gilding on glass, wood, skins, garments, and the metals. All these topics are treated in barbarous Latin, bordering on a species of jargon; some were originally written in Greek, and copied by ignorant scribes in Latin letters, which shows the influence of Constantinople. In one of the sections on ores the word "vitriol" occurs for the first time, being the eighth century, and in the correct significance of an impure ferrous sulphate. A very rational grouping of substances occurs in this work; the minerals and earths are by themselves; then follow gums, rosins, and other products of plants; and thirdly, substances derived from the ocean, such as salt, coral, and mollusks yielding purple dye. A certain recipe for writing in letters of gold is practically identical with one in the Papyrus of Leyden.

A formula for making bronze shows the origin of this name, *De compositio brandisii*, Brindes being a synonym of Brundisium (Brindisi), a town noted in Pliny's days for its metallic mirrors.

A large part of *Compositiones ad tingenda* is reproduced in the work entitled *Mappæ clavicula*, of which the earliest known manuscript dates from the tenth century. This

latter treatise contains recipes for making gold, for multiplying gold, and imitating the precious metal, closely resembling those of the ancient Greek papyri. In this connection cautions are given to conceal the secrets, and an incantation is prescribed to be used during the operation. Exceeding interest attaches to the fact that the use of the hydrostatic balance in analysis of an alloy is clearly described, for this proves that the knowledge of this instrument did not pass through Arabian channels, and possibly came down direct from Archimedes.

The *Liber ignium ad comburendos hostes*, by Marcus Graecus, is one of the most ancient Latin treatises on Greek fire, dating from the twelfth or thirteenth century, and is probably a translation from an earlier Greek work transmitted through Arabian channels. It deals with instructions for making Greek fire, so-called, phosphorescent materials, fire-proofing substances, and the preparation of fuses and petards, composed in part of saltpetre. Greek fire itself, however, dates from the second century, B.C., and phosphorescent stones are named in the much earlier Greek alchemical manuscripts.

Berthelot devotes an interesting chapter to the discovery of alcohol. This product of distillation first appears under the name *aqua ardens*, and the term alcohol in its present signification does not occur before the middle of the fourteenth century; the term *spiritus vini* is also comparatively modern, and *aqua vitae* seems to have been applied to alcohol for the first time by Arnald de Villanova, who died in 1314. The fact that wine yielded an inflammable substance was, however, already noted by Aristotle, but this body was not isolated. Rhases has been given credit for acquaintance with alcohol, but this is erroneous.

The preparation of alcohol by distilling wine is, however, mentioned in a copy of the *Mappea clavicula*, written in the twelfth century, and in the *Liber ignium* of Marcus Graecus.

In attempting to trace to their origin Latin treatises which claim to be translated from Arabic, Berthelot made the important discovery that they are fraudulent, the Arabic manuscripts having no existence. Thus the chemical works attributed to the Arabian physician Jabir ibn Hayyan (Abu Musâ), commonly called Geber, are shown to be fictitious, and the great reverence paid to him as a pioneer in chemistry has been misplaced. The whole history of chemistry has been falsified by giving credit to the Arabians for knowledge which really belonged to a period five hundred years later.

Yet the historical personage Geber, who lived in the ninth century, left many treatises in Arabic, now preserved in Paris and Leyden, and the translation of these occupy 100 pages of the third volume; they are very different from the works so widely known as Geber's, which are found in Latin, French, German, and English.

In like manner the current alchemical treatises ascribed to Raymond Lully are shown to be fictitious, yet his works on philosophy in the Provençal language are extant.

The pseudo-Arabic works in their Latin form contain, however, traces of the ancient Greek alchemical writings, and to endow them with authority the writers referred the text to mythical personages; and as these were cited by later authors who did not doubt their genuineness, the pseudo-treatises acquired undeserved renown. Students of alchemy who have been revelling in the works of Morien, Kalid, Zadith, Mary, and the collection of citations entitled *Turba philosophorum*, are loth to have their antique idols shattered, but this is the fate of every branch of human knowledge when subjected to the modern methods of searching analysis.

The second volume of "La Chimie au moyen âge" has the sub-title, "Syriac Alchemy, comprising an introduction, and several treatises of Syriac and Arabic alchemy from the manuscripts in the British Museum and Cambridge; text and translation."

The existence of Syriac alchemical manuscripts in the British Museum was pointed out to Berthelot by Prof.

Richard Gottheil, of Columbia University, New York City. The most important of these, entitled "The Doctrine of Democritus," was translated from Greek between the seventh and ninth centuries. It begins with a charge of self-purification, followed by a key to the symbols used in the manuscript; these signs resemble in part those occurring in the writings of the earlier Greek alchemists. The first section of the "Doctrine" is called "The Preparation of Gold," the second is called "On the Philosophers' Stone," and the succeeding parts contain a collection of recipes, processes with metals, as well as with sulphur, antimony, arsenic, and ores, analogous to the Leyden papyrus and the *Mappea clavicula*. Rude drawings of apparatus accompany the text. The writer shows acquaintance with a very large number of chemical substances.

The Library of the University of Cambridge possesses a Syriac manuscript, which is a translation of portions of the Greek writings of Zosimus, Democritus, and others. It is similar in character to the preceding.

Volume III. of "La Chimie au moyen âge" has the sub-title, "Arabian Alchemy, comprising an historical introduction, the treatises of Crates, el-Habib, Ostanes, and Djâber, from manuscripts in Paris and Leyden; text and translation."

The Arabic treatises here named are the genuine writings, not the fictitious ones known only in Latin. The first Mohammedan writer on alchemy was Khâled ben Yezid ibn Moaouïa, Prince Omeyyade, who died in 708; he is a historic personage and the reputed teacher of Djâber. Only the titles of his works have come down to us. Djâber, the Geber of the Latins, was, however, the great master of the art and enjoyed the highest reputation throughout the Middle Ages; he is credited with 500 treatises, an Oriental exaggeration. Six of these are here collected and translated. They exhibit evidence of Moslem faith on the part of the author; he shows familiarity with the hydrostatic balance, with many species of minerals (of which an ingenious classification is given), and he discourses on the changes in volume produced by heat and by cold; at the same time he admits using allegorical and obscure language in all his works. There is no reference to the mineral acids, to nitrate of silver, and other chemicals that Geber is supposed to have known. Perhaps the most clever passage in his works is the following from the "Book of Mercy":—

"I saw that persons engaged in attempts to manufacture gold and silver were working ignorantly and by wrong methods; I then perceived that they were divided into two categories, the dupers and the duped. I had pity for both of them."

Berthelot's superb volumes comprise more than 2600 pages, and much of the contents defies review. Besides these original documents, he has published two works dealing in more popular style with the periods of alchemy and Middle Age chemistry. These are entitled: "Les Origines de l'alchimie" (1885), and "Introduction à l'étude de la chimie des anciens et du moyen âge" (1889); the latter is largely reprinted in the quarto volumes; all are charmingly written, well illustrated, and well indexed.

Berthelot had extraordinary qualifications for the task and enjoyed unrivalled opportunities; the result is a magnificent contribution to the history of chemistry, of utmost interest to the chemical student as well as to the philosopher.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 206).

Carbonate of Thallium prepared by Mr. Crookes.—I proceeded to purify this carbonate by the method of suc-

cessive crystallisations. This salt contained sensible quantities of barium, calcium, and sodium, probably in the form of silicates. After six crystallisations, I succeeded in volatilising the carbonate of thallium without finding a trace of the barium or calcium spectra, moistening with chloride of ammonium the platinum spiral used to carry the salt, and introducing it into a hydrogen flame after the thallium had been volatilised. The carbonate, when freed from barium and calcium, showed the sodium line very strongly and persistently. Five re-solutions in pure water, followed by precipitation by absolute alcohol, were not sufficient to prevent the appearance of the sodium line; moreover, on volatilisation it left a small, very fusible, solid residue, which coloured a hydrogen flame yellow, and showed, on spectrum analysis, the sodium line only. I was obliged, from want of material, to abandon my efforts to obtain, from the carbonate sent me by Mr. Crookes, this thallium salt in such a state of purity that it would not show the sodium line. I took up this subject again, using carbonate prepared by myself.

Mr. Crookes's Metallic Thallium.—I checked the preceding results by means of some of the metal prepared by Mr. Crookes. I submitted Mr. Crookes's metal, and some commercial metal I obtained, to the same treatment, as follows:—The thallium to be purified was dissolved in dilute nitric acid, and the solution evaporated to dryness in a porcelain dish. The residue was converted into sulphate by means of a proper quantity of pure sulphuric acid. The resulting salt, consisting of a mixture of thallous and thallic sulphates, was heated to dryness in a platinum vessel. I dissolved the residue in boiling water, and passed a current of sulphurous acid into the solution, which was kept at a high temperature, until it emitted a strong smell. Under the influence of the sulphurous acid, the liquid, which was clear, became very much clouded, forming a white precipitate consisting entirely of sulphate of lead.

After completely cooling, the solution, diluted with water to re-dissolve the sulphate that had crystallised, was filtered, and the clear liquid was heated, and kept at boiling-point until the sulphurous acid was completely eliminated. This result being obtained, I added sulphuric acid; this coloured it a deep brown. When put into a closed flask and left alone, it lost its colour, depositing a black sulphide, consisting of a mixture of sulphides of lead, mercury, silver, thallium, cadmium, and zinc. I saturated the clear liquid in the cold with sulphuric acid; it no longer became coloured, even after twenty-four hours' exposure to light in a closed vessel, and it deposited nothing. The sulphuric acid was driven off by the action of heat, and the sulphate, when re-cooled, was poured into a slight excess of hydrochloric acid to precipitate the thallium.

The chloride produced was washed, first by decantation with water containing 6 per cent of its volume of hydrochloric acid, and then with a wash-bottle, using the same liquid.

The mother-liquor and the washings were evaporated, and the residue examined; it contained a notable amount of zinc, with traces of cadmium and iron.

Thallous chloride when washed as well as possible, still retains sulphuric acid; therefore it may also contain sulphate of zinc, &c. I therefore converted it into sulphate by heating it in a porcelain dish with a suitable quantity of pure sulphuric acid. The salt thus obtained was in the form of monothallous sulphate; I heated it in a platinum dish so as to reduce it to bithallous sulphate. I found that this conversion required great care, because very considerable quantities of thallium might be carried off with the sulphuric acid fumes, and make the air unbreathable.

The thallous sulphate was taken up in boiling water, and the solution again poured into an excess of hydrochloric acid. The chloride deposited on quickly cooling was washed as before, and again transformed into thallous sulphate, and this in its turn into thallous chloride. I

repeated this transformation a third time, because I found a sensible quantity of zinc in the residue left after evaporating the mother-liquor of the second precipitation and the washings from the thallous chloride.

I re-converted the chloride from the third precipitation into thallous sulphate. The transformation of monothallous into bithallous sulphate having had to be effected in platinum, and this metal being slightly attacked by monothallous sulphate, the salt obtained contained a sensible quantity of platinic sulphate.

To eliminate this last metal, I had recourse to the successive actions of sulphurous and sulphuric acids. With this object I kept the solution of thallous sulphate, with the addition of sulphurous acid, at about 100° for several hours. After having thus reduced the platinic sulphate into platinoso-platinic sulphate, which could be precipitated at once by sulphuric acid, I drove off the excess sulphurous acid by heating it, then adding sulphuric acid.

The solution was coloured brown; it was kept on a bath at 100° in a closed flask, until the liquid became colourless owing to the separation of the platinoso-platinic sulphide: this took place slowly, but completely, carrying off a sensible amount of thallous sulphide.

After it became colourless, I filtered the sulphate solution, and heated it to drive off the dissolved sulphuric acid.

It appears, then, that the separation of foreign metals from thallium is a laborious and very delicate operation.

The examination to which I subjected the solution of thallous sulphate enabled me to detect the presence of alumina and soda, due undoubtedly to the attack on the porcelain dishes used during the transformation of the chloride into thallous sulphate. I eliminated the alumina by means of pure ammonia, and then had recourse to successive crystallisations of the sulphate in order to get rid of the sodium. It needed five crystallisations, removing the mother-liquors each time and washing it, before the sodium line was no longer visible in the spectrum of the salt obtained.

I used the sulphate produced thus to obtain:—

- 1st. Metallic thallium. For this purpose I had recourse to electrolysis of the ammoniated solution, as I mentioned before.
- 2nd. Brown or black thallic hydrate.
- 3rd. Thallous chloride, precipitated and then re-dissolved three times in boiling water; immediately after its preparation it showed no trace of the sodium line.
- 4th. Thallous bromide. I find that there are three very distinct physical states of this bromide: the first is white; it is formed when an excess of thallous sulphate is precipitated by hydrobromic acid: the second is pure yellow, but very light; it is formed when dissolved thallous sulphate is poured in the cold into an excess of dilute hydrobromic acid: the third is a slightly yellowish white; it is formed when either white or yellow bromide is dissolved in boiling water, or when either of these bromides is exposed under water to direct sunlight.

Light has no decomposing action on thallous bromide, at least when it does not contain bromide of silver. Immediately after its formation and washing, it shows, on spectrum analysis, no trace of the sodium line; it is the same, in this respect, if it is kept under water in a closed vessel. When left in free air, it shows the sodium line on spectrum analysis after a few days.

- 5th. Iodide, by double decomposition with pure iodide of ammonium. Iodide obtained by pouring a solution of iodide of ammonium into an excess of dissolved thallous sulphate is yellowish white, unaltered by light; it contains sulphate mixed with it, and a long digestion in water at 100° cannot entirely remove it. Iodide produced by pouring a solution of thallous sulphate into an excess of iodide of ammonium is dirty yellow,

unaltered by light; it also contains thallos sulphate: this can be separated by allowing it to remain in the cold in a dilute solution of iodide of ammonium. After long-continued action of iodide of ammonium, it is a more pronounced and purer yellow. When washed then with water, and introduced into a hydrogen flame, it shows the thallium spectrum only. When left in the air under a bell-jar, it shows the sodium line after a few days.

From the metallic thallium obtained by electrolysis of sulphate that had been submitted to *five* successive crystallisations, removing the mother-liquor each time, I procured:—

1st. A solution of thallos hydrate. I prepared this hydrate by exposing well-washed, crystallised, and sodium-free thallium to the action of purified air and water, in a covered platinum crucible, under a bell-jar. The metal, being *half* covered with water, was at first very bright, but tarnished rapidly, and at last was quite black; after a few days it had completely disappeared. At the bottom of the colourless and very alkaline liquid was a small quantity of hydrate of the black trioxide. The thallos hydrate solution showed, on spectrum analysis, persistent signs of the presence of sodium in the flame, although the colour imparted to it by the hydrate was remarkably pure in tint and characteristic of the thallium flame.

It was impossible to evaporate the solution to dryness in platinum or gold without attacking those metals.

2nd. Dissolved and crystallised thallos carbonate. To prepare this salt, I left some thallium under a bell-jar, in air containing carbonic acid, half immersed in pure water in a covered platinum vessel. The metal is entirely transformed into carbonate, which dissolves completely if there is enough water. The solution is colourless, and although prepared from metal, water, and carbonic acid, which show no trace of the sodium line, yet it shows persistent signs of the presence of sodium, doubtless occluded from the air in the bell-jar.

It is sufficient to precipitate the carbonate first by absolute and then by dilute alcohol, and to wash it thoroughly with alcohol at 90°, in order to obtain a powdery salt, which can be entirely volatilised without showing the slightest trace of the sodium line.

I will repeat here what I have already mentioned—the absence of the sodium line is no proof of the absence of sodium from the carbonate.

Crystallised or powdery pure carbonate of thallium is colourless, and may be exposed to direct sunlight without becoming coloured. When left for several days in air under a bell-jar, it shows unequivocal signs of the presence of sodium.

3rd. Dissolved and crystallised thallos nitrate. I obtained a solution of this salt by treating the pure metal with nitric acid distilled directly into a recently-heated platinum vessel. The solution, immediately after its production, showed no trace of the sodium line. When left to evaporate under a bell-jar by the side of a dish of sulphuric acid, it forms colourless prisms, unaltered by air and light. These prisms, when introduced into a hydrogen flame, give absolute indications of the presence of sodium.

The aqueous solution of crystallised nitrate, when poured into pure absolute alcohol, yields, after being properly washed with alcohol at 90°, a powdery precipitate which, when introduced into a hydrogen flame, shows, on spectrum analysis, no trace of the sodium line.

The phenomena shown by all the thallium compounds mentioned above, corroborate the observations made on the presence of sodium in air, and the condensation of it

by bodies which are exposed to it for a certain time. Thus thallium compounds condense it by contact with air like every substance I have carefully examined.

(To be continued).

ON THE QUANTITATIVE ESTIMATION OF TIN.

By CECIL J. BROOKS.

THE following is a brief record of experiments made in the laboratory of Messrs. Stanger and Blount to ascertain the cause of the low results which are often obtained in the determination of tin.

Pure tin being difficult to procure, a good sample of the commercial material was used, which gave the following composition on analysis:—

Tin	99.25 per cent.
Lead	0.36 „
Copper	0.10 „
Iron	0.06 „

Fifty grms. were treated with a small quantity of hydrochloric acid, to avoid the formation of stannic compounds and the solution of impurities; this was kept as a stock solution of approximately known strength; a dilute solution was prepared from this, and was standardised by evaporating 50 c.c. with excess of sulphuric acid, oxidising with nitric acid. Evaporating again with sulphuric acid, and igniting in a gas muffle until the weight of the residue (stannic oxide) was constant, giving a total weight of 0.4508 grm., *i. e.*, 0.00901 grm. of stannic oxide per c.c.

Experiment I.—50 c.c. of the solution were acidulated with hydrochloric acid, and a large volume of hydro-sulphuric acid added; the gas was then passed for some time; finally the solution was heated, filtered, and the precipitate of stannous sulphide washed until the washings were no longer acid, dried, and ignited slowly. As the filter-paper burned, the precipitate broke up with some violence; and after ignition in the muffle gave 0.4467 grm. stannic oxide, the loss being therefore 0.0041 grm. (of stannic oxide).

Experiment II.—50 c.c. were taken, about 10 c.c. of nitric acid (sp. gr. 1.42) added, and the mixture was boiled and precipitated as in Experiment I. It was found that no oxidation had taken place; after the precipitate weighed 0.4451 grm., the loss being in this case 0.0057 grm.

As it was seen from this that oxidation with nitric acid did not take place readily, some of the solution was boiled with acid of different strengths, and it was found that oxidation depended on the dilution rather than on the quantity of acid present.

1. A solution measuring 105 c.c., and containing 0.035 grm. of tin, was boiled with 1 c.c. of nitric acid (sp. gr. 1.42), and gave no indication of oxidation when precipitated with hydrosulphuric acid, the bulk of the precipitate being stannous sulphide.

2. A solution of 55 c.c., and containing 0.035 grm. of tin, when boiled with 1 c.c. nitric acid, gave no indication of oxidation.

3. A solution of 25 c.c., and containing 0.035 grm. of tin, when boiled with 1 c.c. nitric acid, showed partial though slight oxidation.

Bromine was found to be a more effective oxidising agent. Potassium chlorate and hydrochloric acid also acted readily.

My attention was now directed to the possible volatilisation of stannic sulphide on ignition. A specimen was therefore prepared. It was noticed that the thin cakes of stannic sulphide left on drying on the filter, broke up violently when gently heated; in fact, the warmth of the hand was sufficient to cause them to decrepitate.

The sulphide was finely powdered, and heated in a porcelain tube attached to a long glass tube, so that any volatile products (other than sulphur dioxide) might be caught. Oxidation was performed by means of a slow stream of air; the temperature ranged from well below redness to about the melting point of gold. At the close of the experiment it was found that 5.5 per cent of stannic oxide had been volatilised.

It is clear that the ease with which stannic and stannous sulphides are volatilised on roasting is the cause of the difficulty often experienced in the determination of tin, and to overcome these difficulties the following process was adopted:—

Fifty c.c. were acidulated and oxidised with bromine, whilst hot hydrosulphuric acid was added, and the gas passed. The solution was filtered and the precipitate washed, dissolved off the filter with hot ammonium sulphide; the solution evaporated in a weighed basin to a convenient bulk, oxidised with nitric acid, and the residue (stannic oxide) dried, ignited, and weighed.

First determination gave 0.4495 grm. stannic oxide.

Second " " 0.4519 "

These numbers show a fair concordance with the weight taken as a standard, 0.4508 grm. of stannic oxide. As a final test, 0.25 grm. of the same tin was taken and treated as above; and after the subtraction of impurities present in the stannic oxide (lead being calculated as sulphate and copper as oxide) the following result was obtained:—

Tin found.	Calculated.
0.2490	0.2489

The method, though lengthy, appears to be accurate.

REMARKS ON THE LIQUEFACTION OF HYDROGEN, AND ON THE USE OF VACUUM VESSELS.

By Dr. H. KAMERLINGH ONNES.

AFTER referring to the work of MM. Solvay, Cailletet, and Dewar, on liquid hydrogen, and of Van Marum, who first succeeded in liquefying one of the permanent gases, the author mentions that "The temperature to which the hydrogen can be cooled, and the quantity available per unit of time being given, the most advantageous construction of the apparatus to cool the hydrogen further by its own expansion can be studied by means of a model, using a more suitable substance at a more convenient temperature, and applying my theorem concerning Van der Waals' law of corresponding states."

By applying this theorem he shows that the reversing point of the sign of the specific heat of saturated vapour is not in general found at corresponding temperatures in different groups of substances. The author then points out that the application of this theorem to the design of apparatus for liquefying hydrogen presents certain practical difficulties. "For instance, gravity is no corresponding force for two substances in corresponding states. The mutual accelerations by the effect of the molecular forces of two pairs of molecules of substances in corresponding states, when these pairs of molecules are in conform situations, will be expressed for each pair by the same number, when measured with the unit of acceleration proper to the system. But the acceleration of gravity will in general be represented by different numbers when measured in the two cases by the said units, and the similarity in the motion will be disturbed. The theorem therefore can only strictly be applied if the influence of gravity (and accordingly also the influence of convectional transport of heat) is to be neglected.

"And, lastly, it will not be possible in general to obtain walls of such conductive power and such specific heat

that these can give off corresponding quantities of heat in corresponding times.

"Still with these restrictions it can be of use, in the questions we have in view, to consider the gas in the machine as part of the machine itself."

After describing his own apparatus, which led to no good results, and comparing it with Solvay's apparatus, which was designed on similar principles and was also unsatisfactory, the author comes to Linde's method, in which the gas flows from a compressor under high pressure, along a regenerative coil and through a reducing valve, where it does work against the molecular forces, and is accordingly cooled, and then returns by the regenerative coil to the compressor. Now according to the theory published by Van der Waals in 1873, applicable to the ordinary temperature, the Linde apparatus, instead of cooling, should heat hydrogen gas streaming through the reducing valve.

After considering the effect of introducing this gas at low temperature into the apparatus, Prof. Waals has given a new value for the molecular attraction, viz.—

$$a_k e^{\frac{T_k - T}{T_k}},$$

where a_k is a constant, T the absolute temperature, and T_k the critical temperature of the substance, so that " a " increases when the temperature decreases. This theorem predicts, for hydrogen and low temperatures, a relatively great molecular potential energy, and consequently a sensible cooling, in Joule and Thomson's experiment, and a good working of the Linde apparatus. After a pretty full description of the working of a Linde apparatus, the author enlarges on Prof. Dewar's work, which he evidently considers of great importance.

Prof. Dewar, he mentions, begins with much higher pressures than Linde, and expands his gas down to the ordinary pressure, thus wasting still more power than Linde, and departing still more from the theoretically most favourable cooling process, with even better results.

He goes on to say, "In my boiling-glass, just as in Dewar's apparatus, the supply-coil has a cock at the end, and is wound round the cock supporter. This part of my apparatus is also immersed in the gas flowing away. What is blown away from the jet as liquid must serve to cool the supply-coil, and further to take away heat that would otherwise find its way to the bath of liquid oxygen. But in the supply-coil the oxygen is already in the liquid state.

"The spiral was therefore shortened to only such length as seemed necessary to catch the liquid blown away, and to utilise the evaporation of this liquid to cool the adding coil. Dewar, on the contrary, has not been discouraged by the less economical employment of gas, and, armed with his vacuum vessel that leaves the returning gas wholly disposable to cool the coming gas, has directed his attention exclusively to the lowering of the temperature. He succeeded in this manner even in freezing oxygen by means of his hydrogen spray—a splendid outcome of his prosperous researches."

After applying the theorem of the corresponding states of Van der Waals to calculate the quantity of hydrogen that may be expected to be reduced to the liquid state in this apparatus in a certain time, the author mentions Dewar's vacuum vessels, which he states to be the most important addition since 1883 to the appliances for low temperature research.

"The vacuum jackets make it easy to work with liquid oxygen in a different room from where the cryogenic apparatus is placed, and enable one to do this even in other laboratories. . . . In many cases vacuum jackets can also be used to improve the construction of my boiling-glass, in making the evaporation of the bath less than it is without this appliance."

After suggesting some further uses to which the vacuum jackets might be applied, the author concludes by hoping that practical engineers will soon feel the want of these

non-conducting mantles; for, as he says, "As soon as this stage is reached, numbers of heads and hands are disposed to take over the problem from the scientific researcher."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Anniversary Meeting, March 26th, 1895.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

THE PRESIDENT commenced his address by alluding to his early connection with the Society as one of its Secretaries in 1865, when the meetings were held in the buildings of the original Burlington House, and mentioned the fact that it was during his period of office that the change to the present rooms was made. He touched upon the original intention of the Society to found a Chemical Museum, an idea ultimately abandoned; and on the use of the preparation room attached to the meeting room.

Allusion was made to the increased interest attaching to communications illustrated experimentally, and to some of the communications made during the past year which had been so illustrated.

The difficulty arising from the large number of papers now received for reading at the meetings was mentioned, and means were suggested by which this difficulty might partly be met.

The fees for composition, which were unduly low, had now been put on a proper basis.

The communications which had passed between the Council and their French neighbours and colleagues, first on the occasion of M. Pasteur's death, and again on the celebration of the hundredth anniversary of the *Institut* were mentioned.

The decision of the Council to publish a Collective Index of the publications from 1873 to 1892 in two volumes was referred to, and the hope was expressed that both volumes would be delivered to the Fellows entitled to them during the coming year.

Reference was made to the private issue of lists of names calling attention to some of the candidates proposed for election. The feeling of the Council was strongly adverse to the issue of such anonymous appeals.

The arrangements for the publication of the *Proceedings* at the Jubilee of the Society which had been drawn up, and to a large extent completed, by Dr. Armstrong, were mentioned. The record will, it is hoped, consist of two volumes; the first of which, containing a report of the speeches made at the Jubilee meeting and at the dinner which followed, and an account of the early history and development of the Society, is all but complete. The second would consist of an account, written by Dr. Armstrong, of the scientific work of the Society during the first fifty years of its existence.

The Society has lost two of its Foreign Members, Lothar Meyer and Pasteur. A memorial lecture in connection with the former will be delivered by Professor Bedson, on May the 28th; and arrangements are in progress for the delivery of a similar address in connection with Pasteur. Reference was made to Professor Fitzgerald's address on the life and work of von Helmholtz, to the forthcoming celebrations in connection with the completion of Lord Kelvin's fiftieth year as Professor of Natural Philosophy in the University of Glasgow, and to the seventieth anniversary of the birth of Cannizzaro.

It was pointed out that the action of the new by-law under which Fellows whose last year's subscription was in arrear were removed from the register, had tended to keep down the numbers of the Society.

The numerical strength of the Society was as follows:—

Number of Fellows, March 31st, 1895	1979
since admitted	116
reinstated by Council	9
	<hr/>
	2104

Removed on account of non-payment of three annual subscriptions	28
Do. two annual subscriptions	19
Withdrawn	23
Deaths	15
	<hr/>
	85

Number of Fellows, March 31st, 1896	2019
Foreign Members	28

The Society was fortunate in having been deprived of only fifteen of its Fellows by death:—Cave, Herbert; Davy, S. H. M.; Galloway, R.; Kelly, J. A.; Liepmann, Hy.; Linford, J. S.; Looker, P.; McRoberts, G.; Morgan, Wm.; Offord, J. A.; Pochin, H. D.; Smith, C. H.; Smith, M. H.; Winstone, A. B.; Wood, John.

Twenty-two Life Members have not responded to requests for their present addresses, and it has been decided that if a renewed effort to reach them is unsuccessful their names will be removed from the register. Their names are:—Bell, P. C.; Bosanquet, R. H. M.; Brown, Prof. F. D.; Chester, E. D.; Cowie, T. R.; Crampton, Geo.; Custance, Prof. J. D.; Danson, J.; Edwards, J. B.; Emmons, H.; Frost, R.; Hadkinson, J.; Marsh, C. W.; Newton, H.; Strangman, J. P.; Tomlin, A.; Tookey, C.; Watson, W. H.; Williams, T.; Young, B.; Millar, James; Vacher, Arthur.

The number of communications made to the Society during the year was 163.

One hundred and sixteen papers were published in the *Transactions* for 1895, occupying 1172 pages, whereas in the preceding year 83 papers were published, occupying 1039 pages.

The following were the statistics relating to the Abstracts:—

PART I.		Pages.	No. of Abstracts.
Organic Chemistry	692	1190	
PART II.			
General and Physical Chemistry		318	
Inorganic Chemistry		234	
Mineralogical Chemistry		97	
Physiological Chemistry		174	
Chemistry of Vegetable Physiology and Agriculture		110	
Analytical Chemistry		359	
		<hr/>	
Total in Part II.	544	1292	
		<hr/>	
Total in Parts I. and II.	1236	2482	

The Index to the *Transactions*, *Proceedings*, and *Abstracts* occupies 175 pages.

As showing the use made of the Library, it was announced that 675 volumes were borrowed from it. 134 books, 504 volumes of periodicals, and 105 pamphlets were added to the Library.

A new system of registration has been adopted, which, it is hoped, will prevent any further loss of books.

Dr. GLADSTONE, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed.

Professor DIXON, F.R.S., seconded the motion, which was carried by acclamation.

The PRESIDENT having thanked the meeting, Professor THORPE, F.R.S., the treasurer, gave an account of the balance sheet, which he laid before the Society, duly audited.

The receipts had been:—By admission fees and subscriptions, £4454; by sale of Journal and advertisements, £511 8s. 3d.; and by dividends on invested capital, £381 15s. 9d. The expenses had been:—On account of the Journal, £2858 10s. 6½d.; on account of the Proceedings, £261 6s. 2½d.; on account of the General Index, £184 2s. 6d.; on account of the Library, £306 17s. 4d.; the total expenditure being £4406 18s. 2d. Grants amounting to £180 had been made to the Fellows from the Research Fund during the year.

Mr. TYRER proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Mr. D. HOWARD, and carried.

The TREASURER, in responding, proposed a vote of thanks to the auditors.

Mr. A. BLOXAM seconded the motion, which was unanimously adopted, and acknowledged by Mr. B. BLOUNT.

Dr. RUSSELL, F.R.S., proposed a vote of thanks to the Officers and Council.

Professor TILDEN, F.R.S., seconded the motion, which was unanimously adopted.

Professor THOMSON responded.

Professor MCLEOD, F.R.S., proposed a vote of thanks to the Editor, Sub-Editor, and Abstractors, which was seconded by Dr. THORNE, and carried.

Mr. GROVES, F.R.S., responded.

Dr. J. Voelcker and Mr. Nagel were appointed scrutators, and a ballot was then taken for the election of Officers and Council for the ensuing year. The following were subsequently declared duly elected:—

President—A Vernon Harcourt, M.A., LL.D., D.C.L., F.R.S.

Vice-Presidents who have filled the office of President—Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, LL.D., Ph.D., F.R.S.; A. Crum Brown, D.Sc., M.D., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Lord Playfair, K.C.B., Ph.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents—Horace T. Brown, F.R.S.; James Dewar, M.A., LL.D., F.R.S.; Francis Robert Japp, M.A., Ph.D., LL.D., F.R.S.; Ludwig Mond, F.R.S.; W. Chandler Roberts-Austen, C.B., F.R.S.; William A. Tilden, D.Sc., F.R.S.

Secretaries—John M. Thomson; Wyndham R. Dunstan, M.A., F.R.S.

Foreign Secretary—Raphael Meldola, F.R.S.

Treasurer—T. E. Thorpe, LL.D., F.R.S.

Other Members of Council—P. Philips Bedson, D.Sc.; Bennett Hooper Brough; Bernard Dyer, D.Sc.; Otto Hehner; Herbert McLeod, F.R.S.; H. Forster Morley, M.A.; G. Harris Morris, Ph.D.; James Wyllie Rodger; W. A. Shenstone; Arthur Smithells, B.Sc.; Thomas Stephenson, M.D.; Sydney Young, D.Sc., F.R.S.

CORRESPONDENCE.

COLOUR OF THE IONS AS A FUNCTION OF ATOMIC WEIGHT.

To the Editor of the Chemical News.

SIR,—Your abstract of a paper from the *Zeit. Anorg. Chemie*, by Julius Thomsen (CHEMICAL NEWS, vol. lxxiii., p. 198), gives one to understand that a proposal has been made to reject the present form of the periodic classification of the elements, and also that another form of it has been proposed based on the colour of the ions. Will you permit me to say that, after giving years of study to the relations which exist between the colour and chemical

constitution of bodies, many of my contributions to the subject having appeared in this journal, I am in the habit of dilating on Carnelley's Periodic Law of Colour as one of the grandest examples in support of the natural or periodic classification of the elements in its usual textbook form. Here colour is directly seen to be a function of atomic weight, and it is a property that does not want weighing or laboriously ascertaining for the purpose. I am dealing with this matter fully in my work on "The Old Light and the New" (Chapman and Hall, Ltd.), now in the press, and also with its bearing on X-ray phenomena.—I am, &c.,

WILLIAM ACKROYD.

NOTICES OF BOOKS.

Comparative Cost in Chile of Gas and Electricity, and Systems for the Distribution of Energy. ("Koste Komparatibo en Chile del Gas i de la Elektrizidad komo Sistemas de Distribuzion de Enerjia.") By A. E. SALAZAR and K. NEWMON. Santiago de Chile. 1896. 8vo., pp. 72.

THIS pamphlet reminds us of our old acquaintance the "Fonetic Nuz." It is written in a "reformed" version of orthography, and will hence be found somewhat perplexing even to persons by no means ignorant of the Spanish tongue. The authors conclude that in countries like Chile—where gas-coal is scarce, costly, and of mediocre quality, and where good coal has to be imported—an undertaking for the distribution of electric energy, independent and well organised, may be more profitable as a business than that of gas, or for an equality of profit realised may offer to the public a superior commodity at a less price. Coal of ordinary quality may be had at 10 per cent less money than the coal used in the manufacture of gas.

Hydraulic power cannot be had gratuitously in Chile, and its adoption requires a previous comparative study of its advantages as compared with other means of energy.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 14, April 7, 1896.

Observations on the X Rays.—Silvanus P. Thompson.

On Electrified Röntgen Rays.—A. Lafay.—Already inserted.

A Condition of the Maximum Power of Crookes's Tubes.—James Chappuis and E. Nugues.—Already inserted.

Thermic Study of some Oxybromides.—M. Tassilly.—Not adapted for useful abstraction, and not of sufficient importance for insertion in full.

Action of Hydrobromic Acid and Hydriodic Acids upon Phosphonyl Chloride.—A. Besson.—The action of HBr on POCl₃ enables us to obtain the entire series of substitution products, POCl₂Br, POClBr₂, POBr₃, and PBr₅.

On Rice Preserved for upwards of a Century.—M. Balland.—The rice in question is paddy, non-decorticated. The fatty matters tend to disappear, while the acidity was not appreciably modified.

No. 15, April 13, 1896.

On Fallows.—P. P. Dehérain.—The author shows that the practice of fallowing was well adapted to the con-

ditions of former times, but that it has lost its uses since nitrate of soda and generally mixed manures have become available.

On Nitrates in Spring Waters.—Th. Schloesing.—This memoir requires the two accompanying illustrations.

Products of Combustion of an Acetylene Burner. Explosive Mixtures of Acetylene and Air.—M. Gréhan.—If we wish to make use of acetylene we must very carefully avoid the detonating mixtures which it forms with air, and which may occasion disastrous accidents.

On Electrified Röntgen Rays.—A. Lafay.

Action of the Röntgen Rays on Double and Three-fold Electric Layers.—M. Piltschikoff.

Mechanical Action emanating from Crookes Tubes.—A. Fontana and A. Umani.—(See p. 211).

Application of Photography with the Röntgen Rays to the Analytical Research of Vegetable Matters.

Upon Hemolinalol, and on the Constitution of Licareol and Licarhodol.—Ph. Barbier and L. Bouveault.—This memoir does not admit of useful abstraction.

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Society of Arts, 8. (Cantor Lectures). "Applied Electro-Chemistry," by James Swinburne.

— Medical, 8. (General Meeting).

TUESDAY, 12th.—Royal Institution, 3. "Ripples in Air and on Water," by C. V. Boys, F.R.S.

— Society of Arts, 8. "Wood Engraving as compared with other Reproductive Art, and its Future as a Fine Art," by W. Biscombe Gardner.

— Medical and Surgical, 8.30.

— Institute of Civil Engineers, 8.

— Photographic, 8.

WEDNESDAY, 13th.—Society of Arts, 8. "Tunnelling by Compressed Air," by E. W. Moir, M.Inst.C.E.

— Geological, 8.

THURSDAY, 14th.—Royal Institution, 3. "The Art of Working Metals in Japan," by W. Gowland, F.C.S.

— Society of Arts, 4.30. "Tea Planting in Darjeeling," by G. W. Christison.

— Institute of Electrical Engineers, 8.

— Mathematical, 8.

FRIDAY, 15th.—Royal Institution, 9. "Cable Laying on the Amazon River," by Alexander Siemens, M.Inst.C.E.

— Quekett Club, 8.

SATURDAY, 16th.—Royal Institution, 3. "Three Emotional Composers—II. Wagner," by F. Corder, Curator, Royal Academy of Music.

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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1903.

ON THE EXISTENCE OF THE RÖNTGEN RAYS IN ORDINARY SUNLIGHT.

By Dr. T. L. PHIPSON.

SOME readers of the CHEMICAL NEWS may, perhaps, remember that in the year 1881 (June, August, and September) I made some experiments upon a new white pigment containing sulphide of zinc and barium sulphate, and that its extraordinary behaviour with regard to sunlight made me suspect that it contained some compound of a new element, to which I gave provisionally the name of *Actinium*. I did not succeed in obtaining this new element in an isolated form, and circumstances compelled me to abandon the experiments for a time. Anyhow, these experiments proved that there exists in this white pigment some compound on which light acts in a very peculiar manner, as I made known at the time. *Sunlight darkens this compound, but the darkening effect does not occur on those parts of it which are covered with sheets of glass.*

This fact was quite incomprehensible at the time mentioned, and I could put forward no theory to account for so very singular a result. At present it is easy to account for it, by admitting the existence of the Röntgen rays in ordinary sunlight: the white compound which darkens when exposed to sunlight is not sensitive enough to be much affected by light such as will readily affect an ordinary photographic plate; but light which contains the Röntgen rays will affect it and darken it (the dark colour produced becoming bleached again when kept in darkness). Hence I conclude that the Röntgen rays form part of light which reaches us from the Sun, and that it is these rays only which affect the white compound in question.

Perhaps, some day, other compounds will be discovered which act in the same manner towards solar light.

The Casa Mia Laboratory, Putney, S.W.
May 5, 1896.

THE ACTION OF THE RÖNTGEN RAYS UPON DOUBLE AND TRIPLE ELECTRIC STRATA.

By M. N. PILTSCHIKOFF.

SEVERAL physicists have studied the action of the Röntgen rays upon electrified metals; in other words, upon a simple electric stratum. I have also occupied myself with this question (*Comptes Rendus*, cxxii., p. 713), but I have, further, made, in concert with my assistant, M. Totchidlovsky, several experiments upon double and triple electric strata.

I have first observed that a plate of glass, of paraffin, of ebonite, mastic, &c., charged with electricity, either positive or negative, are rapidly discharged by the action of the Röntgen rays, as well if the rays fall upon the charged surface as if they traverse the plate, falling upon the neutral surface. I then undertook to study the action of the Röntgen rays on the charge of a condenser formed by a plate of paraffin (17 c.m. \times 11 c.m. \times 1 c.m.), of a stratum of air (1.8 m.m. in thickness), and of a disc of zinc (diameter, 10 c.m.; thickness, 3.55 m.m.). I first charge the central part of the inner surface of the paraffin plate with negative electricity, and then put the zinc disc in its place. Exner's electroscope, connected metallically with the disc, shows, e.g., -170 volts. I

touch the zinc; the free electricity is dissipated, and there only remains a double electric stratum. I cause the paraffin plate to be traversed by Röntgen rays (issuing from a window of aluminium) during one minute; no measurable loss of the double stratum is produced. I repeat the same experiment, charging the paraffin plate with positive electricity; the same result. Thus the double electric layer is only destroyed by the Röntgen rays very slowly.

If, instead of touching the zinc disc, I leave its charge intact, this charge, according to the law of electric distribution on conductors, occupies exclusively the external surface of the disc, and my condenser in this case possesses a *triple layer* of electricity. The electroscope marking a deviation corresponding to 170 volts, I cause anew the Röntgen rays to fall upon the paraffin plate. In nine seconds the electroscope falls to 85 volts, or the half of its primitive charge, showing that half the free electricity of the triple layer is dissipated in nine seconds. It is easy to demonstrate that it is exactly the free electricity of the zinc which has been dissipated. In fact, if we touch the zinc disc and convey to the earth the rest of the free electricity of this disc, the electroscope will indicate 0 volt. If, then, we take off the disc (which always remains in metallic connection with the electroscope), we observe on the electroscope an initial deviation of +170 volts.

This discharging action of the X rays through a double stratum, which remains almost intact, and through a disc of zinc, which is absolutely opaque to these rays, upon the free electricity of the outer surface of the disc, appears no less unexpected than difficult to explain.—*Comptes Rendus*, cxxii., p. 839.

ON THE RÖNTGEN RAYS ELECTRISED.

By A. LAFAY.

THE experiments on Röntgen's rays electrified which I have already had the honour of communicating to the Academy, give room for an objection which it was necessary to remove.

We may ask ourselves if these rays really undergo a change of nature, an *electrisation*, in traversing the electrified lamella, or if the deviations observed are merely the result of the combined effect of the electro-magnet and of the electric field developed by the silver plate.

To remove this uncertainty, I have repeated the experiments already described, and I have caused the electrified ray, on its issue from the lamella, and before its passage between the keepers of the electro, to penetrate into a Faraday case placed in communication with the earth. The sensitive plate was contained in the interior of the metallic case, which presented merely a small aperture destined for the entrance of the rays. In these conditions, which eliminate as far as possible the effects of the electric field, I have observed the same deviations as formerly.

In order to throw yet more light on the nature of the electrified rays, I have repeated with them the experiment which M. Perrin has performed on the cathodic rays.

In the present case, the execution of the experiment presented no difficulty. For the ball of a gold leaf electroscope I substituted a Faraday's cylinder, the aperture of which is turned upwards. The apparatus, thus transformed, is completely enclosed in a metallic cylinder, the upper opening of which is closed with a leaden cover which has a central aperture. Above this aperture I arrange a silver plate connected to a Wimshurst machine, which serves to electrify the rays sent by the Crookes tube, placed above.

In these conditions, I observed that the Faraday cylinder is charged with electricity of the same kind as that supplied to the electrifying plate. The phenomenon

continues if we substitute for silver a metal leaf of any kind sufficiently thin to be traversed by the Röntgen rays.

We still obtain the charge of the cylinder if we close the aperture in the leaden cover with a transparent dielectric (paraffin, ebonite, paper, &c.); it is no longer the same with an opaque dielectric, such as a plate of glass with a base of lead.

In view of this result, it is natural to demand if a very thin sheet of metal placed in communication with the earth would not equally allow itself to be traversed by the electrified flux, and if the conductivity of the metal would be sufficient to deprive the rays of all their electricity.

It has not yet been possible for me to satisfy myself of this fact by an experiment such as I have just described, but we must remark in the present case the radiation is weakened by its passage through the plate; and that, further, the Röntgen flux, acting as a conductor between this plate and the Faraday cylinder, increases the losses of the electroscope. This is why I purpose, by a method slightly modified, entering upon the investigation of this question, which presents a great interest, and would give the key to the remarkable results obtained by Lenard.

I shall conclude this paper by indicating a very curious fact. In my former communication I had, after the example of Hittorf, assimilated the Röntgen flux to a sheaf of flexible conductive wires. This manner of conceiving the phenomenon occasioned me to modify the experiment already described in the following manner:—

I completely enclosed the photographic plate with leaves of aluminium, then putting the platinum wire and the lead screens in communication with the earth, I have, whilst the electro-magnet was at work, electrified the metallic envelope containing the plate.

In these conditions, the hypothetical filaments of Hittorf permit the efflux of the electricity developed on the aluminium, and should, in consequence, bend in a direction determined by the action of the magnetic field.

The deviations observed have entirely confirmed this view, and I have thus verified—a result at first slightly paradoxical—that it is indifferent for deflecting the Röntgen rays to electrify them before and after their passage across the magnetic field.—*Comptes Rendus*, cxxii., p. 837.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 218).

CHAPTER XII.

THE CHARACTER IMPARTED TO FLAMES, AND TO AN ELECTRIC SPARK OR ARC, BY THALLIUM AND ITS COMPOUNDS.

The Luminous Spectra of Thallium.—It is well known that in March, 1861, Mr. Crookes, when making a spectrum analysis of a flame containing the residue of certain samples of selenium, found in the spectrum of this green flame a very bright green line. He traced the colour of the flame and the appearance of the green line to the existence of a new element, to which he gave the name thallium. On the 16th of May, 1862, the late M. Lamy proved that the element discovered by Mr. Crookes was a metal. The subsequently published works by Mr. Crookes and the late M. Lamy, on the physical and chemical properties of thallium and its compounds, are well known; I have no intention of reverting to that subject here. I will confine myself to mentioning that Messrs. Crookes and Lamy agreed in assigning a single line to the thallium spectrum. At the request of M. Lamy, Messrs. Bunsen and Kirchhoff submitted, early in 1863, the flame charged with this metal to spectroscopic analysis, and found a line which they could not split up when using the large spectroscope used by M. Kirchhoff

during his study of the solar spectrum. They assigned to this single line the number 1442·6 on the scale of M. Kirchhoff's instrument.

About the same time, the late Mr. Miller made a spectroscopic examination of thallium and its sulphate as prepared by Mr. Crookes. When introducing in succession the metal and its sulphate into a hydrogen and into an oxyhydrogen flame, he likewise found a single line.

He also found that Mr. Crookes's metal, when put into an induction spark, showed a more complex spectrum, containing lines characteristic of cadmium, zinc, and lead.

In his work published in 1874, M. Lecoq de Boisbaudran attributed a single line to the electric spectrum of thallium and its compounds; but he gave *two green lines* for the flame spectrum, one very brilliant, the other very faint.

M. Bunsen took up this work again about the same time. The results of his investigations are given in his "Spectral-analytische Untersuchungen." When working on most carefully purified thallous chloride, he found that the flame and electric spectra of this compound each consisted of a single line, the respective positions of which on the scale of his spectroscope he gave.

Lastly, Prof. Liveing, in his work on the ultra-violet spectra of the elements, published in 1883, gave a very complex spectrum for thallium.

These discrepancies decided me to subject the methods of obtaining pure thallium and its principal compounds to a thorough revision, with the object of ascertaining whether the differences noted were due entirely to the want of purity of the materials used by different observers, or whether they could or ought to be imputed either to the method of investigation adopted or to the analysers used.

When undertaking this research, I also wished to ascertain whether it was possible to obtain thallium and its principal compounds in such a state that, when introduced into a flame or an electric spark or arc, they would not show any trace of the sodium line, and whether it was possible, by raising the temperature, to cause the appearance of one of the lines characteristic of potassium, lithium, calcium, strontium, or barium, in the thallium spectrum.

In the last chapter the researches I undertook, for the purpose of obtaining thallium and its compounds of uniform composition, are described. I may refer chemists who wish to study those researches to that chapter; I will limit myself to describing here the spectroscopic studies of the above materials, in the order described in that chapter.

The Flame Spectrum of Sulphate of Thallium prepared by M. Lamy.—I commenced my observations by means of this sulphate, from which I had eliminated all impurities. When introduced into a pure hydrogen flame, it imparted to it a pure green tint. Spectrum analysis of a flame into which sulphate that had been purified, and then crystallised four times in succession, had been introduced, enabled me to see a single line, the well-known green thallium line. On substituting a dark blue coal-gas for a pure hydrogen flame, I found only a single line, but it lacked the intensity of colour of the thallic flame from a well-made Bunsen burner, as well as the pure tint of a thallic flame of pure hydrogen; it appeared to be a mixture of green and blue. The flame was greener in the outer layers and bluer inside.

Sulphate of thallium, when introduced on a platinum loop coated with iridium into a flame of hydrogen raised to incandescence by the admixture of oxygen,—that is, in the blue hydrogen flame,—coloured it a *very much paler* green than hydrogen burning with a dark flame. The same phenomenon occurred with an oxy-coal-gas flame.

When it was introduced into the inner cone of an oxyhydrogen or oxy-coal-gas flame, by means of a fine platinum wire loop coated with iridium, the thallic tint

of the flame was so weakened that it seemed to have disappeared; it was only recognisable at a distance of from 1 to 2 c.m. from the point of contact.

The spectrum of sulphate of thallium in incandescent hydrogen, or in the inner cone of an oxyhydrogen or oxy-coal-gas flame, consisted of the *single* green line. In incandescent hydrogen the spectrum consisted of a *dark* band, on which appeared the single line only.

Thallic rays mask rays from incandescent hydrogen. To ascertain the truth of this fact, it suffices to introduce sulphate of thallium into hydrogen sufficiently incandescent to show a bright continuous spectrum; at the instant of introduction the continuous spectrum is extinguished, and replaced by a dark band showing the single green line. The facts are different when sulphate is introduced into the inner cone of an oxyhydrogen or oxy-coal-gas flame, and this part of the flame is analysed. The single line is distinctly seen, but the spectrum is not dark; a continuous spectrum is seen. When there were two observers, and a third person engaged in introducing sulphate into the inner cone, they could in turn see the background of the spectrum dark, or showing a continuous spectrum with a single line, according as spectrum analysis was made of a part away from the inner cone, or of the inner cone itself. According to the conditions, therefore, the thallic rays could or could not mask the rays from incandescent hydrogen.

Rays from thallic sulphate instantly masked the hydrocarbon spectrum.

When working with thallic sulphate which did not show the sodium line when put into a pure hydrogen flame, burning in pure air, I was unable to cause the appearance of the sodium line by raising the temperature, whether I used an oxyhydrogen or oxy-coal-gas blowpipe. Besides, the experiment is very difficult, on account of the great volatility of the sulphate.

It succeeded best with pure iridium. I arranged a thick layer of this metal on a small piece of pure carbon let into a block of compressed magnesia, and which had been for some time kept at white heat in a pure carbon crucible. After heating the iridium in an oxyhydrogen blowpipe until it became soft, I gradually dropped the sulphate on to it. The thallium line alone appeared, either on a continuous spectrum or on a dark band, according to whether the thallic flame were examined near the point of support or at $1\frac{1}{2}$ to 2 c.m. from it; but in any case *neither the sodium D line nor any other line* appeared.

On introducing a small cone of pure carbon, saturated and completely covered with fused thallic sulphate, into the inner cone of an oxyhydrogen or oxy-coal-gas blowpipe, exactly the same spectrum was seen,—that is, the single green line on a bright or dark background, according to the part of the flame examined. When using the large Hilger spectroscope fitted with its six Iceland spar prisms, the dispersion of which is so great that *seven* lines were easily seen between D_1 and D_2 in the solar spectrum, the thallium line was not split up; this confirmed the observation made in 1863 by Messrs. Bunsen and Kirchhoff; the only change noticed, and one which always occurred, was the decided weakening of the green tint when it was examined against a bright background.

Does the impossibility of seeing the sodium line in the spectrum of thallic sulphate prove the absolute absence of sodium from the vapour submitted to spectrum analysis? The facts I have just mentioned tend to show that this question must be answered with caution. It is an undoubted fact that the thallic sulphate, before being repeatedly crystallised, showed the sodium line strongly and persistently, and that after these repeated crystallisations the sodium line could no longer be detected. It is also certain that sulphate thus freed from any quantity of sodium capable of being detected by spectrum analysis, when left in air under a bell-jar for several days, gave positive signs of the presence of sodium. Having reached this point, it is found that the colour intensity of the so-

dium line is very weak, that the thallic rays have a great influence on this colour intensity, and that they can mask, or at least render invisible, the sodium line, when they have reached a given limit. When one has succeeded in procuring a thallic sulphate which no longer shows the sodium line in hydrogen burning in pure air, and when one introduces this sulphate into a Bunsen flame burning in air, and showing the sodium line, though *faintly*, one notices the instant disappearance of this sodium line as soon as the thallium line appears. If the air is so much contaminated that yellow scintillations appear in flames, as is almost always the case when the air is in motion, the continuous sodium line is seen to disappear, and a weak intermittent sodium line appears. It is evident, then, that thallic rays exercise an extinguishing power over sodium rays. This power, moreover, appears definitely limited as regards sodium, but yet it is sufficient to justify a doubt as to the possibility of ascertaining whether it is possible to procure thallium or a thallic compound absolutely free from sodium.

I discuss the question in a general sense, because I found the same property in all the thallic compounds I have mentioned.

Having verified these facts, I used purified thallic sulphate to prepare metallic thallium and its trioxide and chloride.

I gave all necessary details in the last chapter, to which I refer the reader.

The Flame Spectrum of Thallium prepared from M. Lamy's Sulphate.—Thallium prepared by electrolysis of this sulphate, when introduced into a hydrogen flame or a Bunsen burner, on the end of a fine platinum wire loop, burnt in them with a bright light, and coloured them the same as the sulphate from which it was reduced. Spectrum analysis only showed a single very brilliant green line. I repeated the experiment when the air contained a very sensible amount of sodium, without being able to cause the sodium line to appear on the dark background showing the green line.

Part of the same thallium, when left for three days in dry air, in a well-closed cupboard, occluded from the air enough sodium to show the sodium and thallium lines, when introduced into a hydrogen flame, until the metal was completely volatilised. In hydrogen raised to incandescence by burning in oxygen, the thallium burnt with extreme brightness. When the slit was narrow enough, the spectrum was dark, and showed the single very intense green line. If, on the other hand, the slit were wide enough to show the green line at least 1 m.m. in width, a continuous spectrum appeared between Fraunhofer's C and F lines, and the intensity of the line was greatly diminished. Owing to the bright light, *lines could easily be overlooked*. On two occasions I made spectrum analyses of an oxyhydrogen flame impinging on pure iridium heated nearly to its fusing-point, and on which I had dropped some small globules of thallium. I saw the thallium line alone on a partially continuous spectrum. I was not able to cause the appearance of the sodium or any other lines, or to split the thallium line when using the large Hilger spectroscope with its six prisms, or by means of Rutherford's grating, substituting it for the prism in the Steinheil spectroscope. I made this last experiment with the help of M. Fievez. I am convinced that it is not possible to make a trace of sodium, or *at least to see the sodium line*, at a temperature above the fusing-point of iridium, when the thallium experimented with does not show the sodium spectrum *at a low temperature*.

(To be continued).

Effects of Smoke upon Agriculture.—According to Max Hagen, the smoke of wood-fires is not in the slightest degree injurious to vegetation. — *Chemiker Zeitung*.

A REVISION OF THE ATOMIC WEIGHT OF ZINC.*

FIRST PAPER: THE ANALYSIS OF ZINCIC BROMIDE.

By THEODORE WILLIAM RICHARDS
and
ELLIOT FOLGER ROGERS.

Introduction.

IN an account of a recent investigation on the occlusion of gases by the oxides of metals (*Proc. Amer. Acad.*, xxviii., 200, Richards and Rogers) it was shown that zincic oxide, in common with cupric and magnesian oxides, has the power of retaining important quantities of oxygen and nitrogen gases, even at very high temperatures. Hence it was evident that all determinations of the atomic weight of zinc depending upon the conversion of the metal into the oxide through the ignition of the nitrate must be influenced by a constant error, which has the tendency to make the results lower than the true value. In consideration of this fact, it becomes very important to review all of the results thus far obtained regarding the atomic weight of zinc, in order to determine how seriously the error in question may influence our accepted value. A chronological list† of the accepted data is given below:—

1809.	Gay-Lussac, <i>Mém. d'Arceuil</i> , ii., 174 . . .	65.55
1811.	Berzelius, <i>Pogg. Ann.</i> , viii., 184 . . .	65.57
1842.	Jacquelain, <i>Ann. de Chim. et de Phys.</i> , [3], vii., 204 . . .	66.24
1844.	Favre, <i>Ann. de Chim. et de Phys.</i> , [3], x., 163 . . .	65.99
1844.	Erdmann, <i>Berz. Jahresber.</i> , xxiv., 132; and <i>Pogg. Ann.</i> , lxii., 612 . . .	65.05
1883.	Pelouze and Fremy, " <i>Chem.</i> ," p. 55 . . .	65.07
1883.	Baubigny, <i>Comptes Rendus</i> , xcvi., 906 . . .	65.41
1883.	Marignac, <i>Archiv. Sci. Phys. et Nat.</i> , [3], x., 5, 193 . . .	65.30
1885.	Van der Plaats, <i>Comptes Rendus</i> , c., 55 . . .	?
1887.	Reynolds and Ramsay, <i>J. Ch. Soc. Trans.</i> , li., 854 . . .	65.67
1888.	Morse and Burton, <i>Am. Chem. Journ.</i> , x., 311 . . .	65.27
1889.	Gladstone and Hibbert, <i>J. Chem. Soc. Trans.</i> , lv., 443 . . .	65.44

The various results have been reached:—

1. By converting a known weight of metallic zinc into the oxide (Berzelius, Jacquelain, Erdmann, Morse and Burton).
2. By the evolution of hydrogen from acids by metallic zinc, the hydrogen being either measured or burned (Jacquelain, Favre, Van der Plaats, Reynolds and Ramsay).
3. By the conversion of a salt of zinc into a zincic oxide through ignition (Favre, zincic oxalate; Pelouze, zincic lactate; Baubigny, zincic sulphate).
4. By the determination of the electrolytic equivalent of zinc (Gladstone and Hibbert).
5. By analysis of a haloid salt of zinc (Marignac).

The work of Morse and Burton by the first method is so far superior to the previous determinations made in the same way, that the older ones may be wholly neglected. The two or three possibilities of infinitesimal error, such as the chance that the zinc might contain impurities taken from the glass used for its distillation, may be wholly neglected when compared with the great error due to the occlusion of nitrogen and oxygen. As the amount of this error is dependent upon the physical conditions of the zincic oxide, it is impossible to make an accurate correc-

tion except by the actual determination of the gas in the oxide remaining from the determinations. From our own experiments (*Proc. Amer. Acad.*, xxviii., 200) it would appear that a grm. of zincic oxide obtained from the nitrate usually contains about 0.00057 grm. of occluded gas; upon this basis, Morse and Burton's result would become 65.458 instead of 65.269.

In considering the results obtained by the second method, the results of Favre and Jacquelain may be rejected at once. Of Van der Plaats' results it is necessary to state only that some error must have crept in while recording his data, for it is inconceivable that 6.6725 grms. of zinc should yield only 1.1424 litres of hydrogen. The work of Reynolds and Ramsay was much more careful and detailed; but the results varied very widely. Hydrogen evolved from very pure zinc was measured, with many precautions, but after the rejection of thirty-four experiments eleven more gave a value of 65.24, and still five more gave 65.47 as the atomic weight of zinc. Since the publication of their work many investigations have shown that the density of hydrogen is greater than the value assumed at that time. If a litre of the gas weighs 0.0001 grm. (Lord Rayleigh and others) and the atomic weight of hydrogen is taken as 1.0075 ($O=16.000$) the atomic weight of zinc deduced from Reynolds and Ramsay's experiments becomes about 65.63.

The two older results obtained by the third method are worthy of no further mention. Baubigny's work upon the ignition of zincic sulphate is very interesting, but probably incomplete. It will be remembered that the value for copper obtained by the same method was too low (Richards, *Proc. Amer. Acad.*, xxvi., 275), owing, probably, to the occlusion of sulphuric acid by the cupric sulphate. It is not impossible that a similar error may have crept in here, for the conditions are similar; but it is probable that it is here counterbalanced by the retention of sulphur trioxide by the zincic oxide. In a series of experiments made in this laboratory, pure zincic oxide obtained from the carbonate (as described further on), was ignited to constant weight in an oxidising atmosphere at a temperature above the fusing-point of gold*; it was then dissolved in dilute sulphuric acid, which left no residue upon evaporation, and very gradually brought again to the same high temperature. In no case were we able to expel all of the sulphuric acid which we had added. Three experiments are appended:—

Weight of zincic oxide before. Grm.	Weight of zincic oxide after. Grm.	Gain. Grm.
1.03009	1.03032	0.00023
0.80243	0.80265	0.00022
1.03447	1.03473	0.00026

Average for 1 grm. ZnO. . . 0.00025

Gladstone and Hibbert deposited silver in one cell by means of a voltaic current, while zinc was being dissolved from an amalgamated plate in another. Although the experiments are interesting, it would appear from the results of Vanni (*Ber. d. D. Ch. G.*, xxiv., Ref. 882) and others that the possibility of side reactions makes the strict applications of Faraday's law for the determination of atomic weights of rather doubtful efficacy. One would expect the method adopted to give a result larger than the true one.

Marignac's work upon the chloride of zinc and the double chloride of zinc and potassium is even less satisfactory than his investigations of other chlorine compounds; it merits no further notice.

It is evident from these statements that the three least unsatisfactory determinations are all vitiated to a greater or less extent by constant errors:—The work of Morse and Burton by one which tends to lower the result; the

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*. Presented April 10, 1895.

† Much assistance in preparing the list has been obtained from the works of Clarke, Meyer and Seubert, and others. The results have been re-calculated with the assumption of the following atomic weights:— $O=16$, $C=12.002$, $Cl=35.456$, $Aq=107.93$, $H=1.0075$.

* Four grms. of pure gold melted in fifteen minutes from the time of turning on the air blast in the furnace.

work of Gladstone and Hibbert by one which may tend to raise the result; and the work of Baubigny by two which tend to counteract one another. One would expect the atomic weight of zinc to prove in the end equal to about 65.4.

It seemed very desirable to obtain a series of determinations which should be wholly different from any of these; and for this reason zincic bromide was chosen as the starting point of the present research. Additional advantages presented by the use of this substance are the fact of its ready and accurate analysis, and the fact that a determination of the ratio $2\text{Ag} : \text{ZnBr}_2$ would bring the element into a series of elements which have been determined by Stas and others with great precision in this way.

(To be continued).

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY CONVERSAZIONE, MAY 6, 1896.

On this occasion there were submitted to the Fellows and the visitors a number of most interesting exhibits in illustration of recent discoveries.

"Röntgen's rays" formed the subject-matter of three exhibitions.

In the Officers' Room, Mr. A. A. C. SWINTON gave a practical demonstration of the "New Photography"—a name which we hope is merely provisional.

When a suitable Crookes vacuum tube is excited, the invisible radiations that proceed from the point where the cathode rays strike a solid substance, will impress photographic plates, will cause certain salts to fluoresce, and will discharge electrified bodies.

These radiations pass with ease through various substances which to ordinary light are quite opaque, while they penetrate with difficulty other substances which to light are very transparent.

Since bone is more opaque to these rays than tissue, it is possible by their means to obtain shadow pictures of the bones in the living body either upon a photographic plate or upon a fluorescent surface within a cryptoscope. Similarly other hidden objects, such as the coins in a purse, the contents of closed boxes, and such like, can be rendered apparent.

In the Council Room, Mr. SYDNEY ROWLAND gave a copious and most instructive series of "skiagrams," chiefly with reference to medical and surgical diagnosis.

The following analysis, based on a record of some fifty cases, is useful as showing the branches of surgery in which the new process will probably be found of most use. About 20 per cent of these include the discovery and location of foreign bodies, needles, bullets, &c., lodged in soft tissues, and in one case a coin lodged in the intestine, which caused troublesome symptoms. In one of these cases two previous operations had been fruitlessly performed. 15 per cent of the cases were instances of pathological conditions of the elbow joint of more or less obscurity, on which new and unexpected light was thrown by the diagnosis thus obtained. In 10 per cent of the cases the object in view was the determination of the extent and distribution of tuberculous lesions in bone. Various ankyloses and deformities of the bones and joints of the extremities have made up the remainder of the cases.

In the same room, Mr. HERBERT JACKSON demonstrated the use of phosphorescent substances in rendering the X rays (Röntgen's rays) visible.

The tube used to produce the rays is a slight modification (described in the *Proceedings of the Chemical Society*) of a tube originally introduced by Mr. Crookes to illus-

trate the heating effect of cathode rays. These are brought to a focus at the centre of curvature of the concave cathode, whence they proceed in nearly a straight line to a platinum plate, from the surface of which they are apparently scattered in all directions. The rays penetrating the glass fall upon phosphorescent bodies and are rendered visible, thus showing the different extents of response of these bodies to such rays.

Helium also took a prominent place among the exhibits. In the Principal Library, Mr. F. McCLEAN, F.R.S., exhibited photographs of the spectra of twenty-three of the most characteristic helium stars. It is noted that in 1892 Prof. Lockyer ascribed the peculiarity of the spectra of these stars to the presence of helium.

In the same room, Prof. CLOWES, D.Sc., exhibited a new method of gas-testing in electric culverts.

This apparatus is also suitable for detecting and measuring inflammable gas in inaccessible places in gas works, coal bunkers, coal mines, and furnace flues. It weighs only 11 lbs.

A standard hydrogen flame, fed from a small steel cylinder of the compressed gas, is inclosed in a brass vessel provided with a transparent front. This apparatus is mounted on a camera tripod, and is observed by throwing a black cloth over the head. The air to be tested for inflammable gas is pumped over the flame by dropping the end of a flexible tube into the culvert, and compressing a rubber ball provided with suitable valves. A constant stream of the air is thus caused to pass over the hydrogen flame, and by the appearance and dimensions of the flame-cap produced, gas is detected and its percentage is accurately measured. The hydrogen flame can be adjusted to two standard heights, and thus percentages of gas from 0.2 to 5 can be detected and measured.

In the same room, Prof. HARTLEY, F.R.S., displayed a series of photographs of spectra in illustration of the Bessemer flame, taken at the North-Eastern Steel Co.'s Works, at Middlesbrough-on-Tees.

The series show:—Four photographs of the Bessemer flame seen issuing from the converters, 15 in. by 12 in.

Two plates of spectra of the Bessemer flame, 12 in. by 10 in.

Thirteen spectra (plate 17) taken at intervals during the "blow," and also during the "over-blow." The spectra slightly overlap. This series shows the increase of temperature during the combustion of the carbon. A gallium line is seen in ten of the spectra.

The detection of gallium in the Bessemer flame spectra (plate 24).

Three plates of spectra, 12 in. by 10 in., illustrating the method of detecting gallium by spectrum analysis of substances separated from the metal and ore.

Plate 51, showing—(1) Spectrum of sesquioxide metals separated from 1 kilo. of Cleveland iron ore. (2) The spectrum of an insoluble residue collected on a filter-paper and burnt. (3) Precipitate from the solution of a manganese ore collected on a filter and burnt. It contains indium. Plates 53 and 54 are of a similar description.

Prof. LIVERSIDGE, F.R.S., showed gold nuggets displaying their internal structure. The specimens (Australian) had been sliced and polished, and were then etched with chlorine-water, thus showing the internal crystalline structure and the enclosures of quartz, iron oxide, &c.

In the Secretaries' Room, the Gas Cylinder Committee exhibited the results of experiments on steel gas-cylinders.

These show—(1) The danger of using hard or un-annealed steel for gas cylinders; (2) the extraordinary amount of violent ill-treatment to which a good soft annealed cylinder may be subjected without destruction, even when charged to 120 atmospheres; (3) the effect of very great internal pressure steadily applied, in this case due to the expansion of liquefied ammonia gas which

completely filled the cylinder when cold; (4) the violently destructive character of the explosion of mixed gases under pressure which no practicable cylinder can withstand.

Prof. WORTHINGTON, F.R.S., and Mr. R. S. COLE exhibited instantaneous photographs of splashes.

These photographs were taken each with an electric spark giving an exposure of less than 3-millionths of a second. The spark could be so timed as to pick out any desired stage of the splash within limits of error not exceeding, as a rule, about 2-thousandths of a second. In this way the progress of a great variety of splashes has been followed in minute detail. Specially interesting are those which illustrate the formation of a bubble, and those which show how the nature of the disturbance produced by the entry of a solid sphere depends on the condition of its surface. The motions set up even by a smooth sphere are difficult of explanation.

Prof. ROBERTS-AUSTEN, C.B., F.R.S., showed modifications of an experiment of M. Charles Margot by Professor Roberts-Austen, C.B.

A wire of aluminium is raised, by a current of 30 ampères, to a temperature far above the melting-point of aluminium, but a film of oxide on its surface prevents the wire from breaking. The molten wire through which a current is passing, may then be attracted by a magnet.

Mr. J. NORMAN LOCKYER, C.B., F.R.S., exhibited—

1. Flint glass prism of 9 inches aperture and 45° refracting angle.—The prism has been constructed by the Brothers Henry, of the Paris Observatory, and will be used as an objective prism for photographing the spectra of stars.

2. Photograph showing positions of coronal spectrum rings in the total eclipse of the sun, April 16th, 1893.—The original negative was taken by Mr. Fowler, at Fundium, West Africa, with the 6-inch prismatic camera near the middle of totality, with an exposure of forty seconds. In addition to the images of a number of prominences, there are portions of rings representing the radiation spectrum of the corona. The brightest of the rings corresponds to the well-known corona line 1474 K, but the others have not been previously photographed. All the rings are most intense in the brightest coronal regions, near the sun's equator.

3. Photographic spectra of α Cygni, γ Cygni, and Arcturus.—The photographs were taken at South Kensington with a 6-inch objective prism of 45° , and illustrate the difference between stars of increasing and stars of decreasing temperature. Arcturus is a cooling star, almost identical with the sun, while α Cygni differs very widely from the sun and is getting hotter. The spectrum of γ Cygni, like that of Arcturus, consists of a very large number of lines, but as many of the more prominent lines agree with those of α Cygni, and are absent from the solar spectrum, this star must be classed with those of increasing temperature.

4. Photographs showing the spectra of helium and gas X in relation to the spectra of Orion stars.—The lines of the two gases are arranged in the series deduced by Messrs. Runge and Paschen, and their distributions in the spectra of Bellatrix, Rigel, δ Orionis, and Spica are shown.

5. Photographic map of the spectra of metals of the iron group.—The map extends from wave-length 3900 to 5900, and includes the spectra of iron, manganese, cobalt, nickel, chromium, and uranium, as shown at the temperature of the electric arc. Rowland's map of the solar spectrum forms the term of comparison, so that the wave-lengths of the lines can be read off directly from the map.

In the Meeting Room, Prof. MELDOLA, F.R.S., exhibited, on behalf of Prof. Lippmann, a series of colour photographs by the interferential method.

And at 11 o'clock Prof. DEWAR, F.R.S., showed some brilliant experiments with liquefied air and oxygen.

CHEMICAL SOCIETY.

Ordinary Meeting, April 23rd, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MESSRS. J. W. Helps, B. Bernard Turner, C. Edward Sage, were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Robert Addie, Langloan Iron Works, Coatbridge, N.B.; Samuel William Allworthy, M.A., 32, Lonsdale Terrace, Belfast; John Caley, 41, Norfolk Street, Beverley Road, Hull; Charles Matthew Crossman, B.Sc., 23, Euston Buildings, N.W.; Ralph Hamilton Hanger, Riverslea, Stoneferry, Hull; William Arthur Finch Lethbridge, Ivy Cottage, St. David's, Exeter; Cecil Rudolf Lidgey, 43, Marmora Road, Honor Oak, S.E.; William McConnell, jun., 25, Percy Gardens, Tynemouth; James Stanley Muir, 27, Huntley Gardens, Glasgow; James Haddon Overton, 15, West Street, Banbury; Hastings Montagu Page, Poona; Arthur Payne, 12, Victoria Square, Newcastle-on-Tyne; George Egerton Scott Smith, 67, Surrey Street, Sheffield.

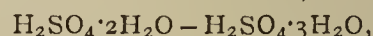
Of the following papers those marked * were read:—

*51. "*The Constitution of the Cereal Celluloses.*" By C. F. CROSS, E. J. BEVAN, and CLAUD SMITH.

The general bearings of the subject, of which this is a special part, have been dealt with in previous communications (*Trans.*, lxx., 472; lxxvii., 433; *Ber.*, 1893, 2520; 1894, 1061; 1895, 1940 and 2604; *J. Amer. Chem. Soc.*, 1896, 8).

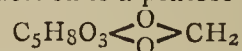
It is now shown that the cereal celluloses may be resolved by acids into soluble derivatives of their furfuroid constituents, leaving a residue of a normal cellulose, and a process has been devised which sharply effects this separation.

Two methods of hydrolysis have been studied:—(1) treatment with acids of the series,—



in the cold, dilution and filtration from re-precipitated cellulose, the furfuroid remaining in solution; (2) treatment with dilute sulphuric acid, 1 to 2 per cent strength, at 1 to 9 atmos. steam pressure. The best results are obtained on short heating (15 mins.) at 3 atmos. The furfuroid is then obtained quantitatively.

From a study of composition, cupric reduction, yields of furfural, yields, composition, and properties of osazones, and certain special oxidations, it is concluded that the furfuroid in question is a pentose monoformal,—

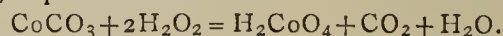


Such a compound, having the empirical formula of a normal cellulose, could arise within a cellulose complex by transformation of the terminal, CH_2OH , of a hexose molecule; *i. e.*, an oxidation by internal re-arrangement. The formaldehyde residue thus produced is not split off, but remains united by oxygen with the pentose residue which is simultaneously produced.

*52. "*On a New Compound of Cobalt, and a Rapid Method of detecting Cobalt in presence of Nickel.*" By R. G. DURRANT.

The author shows that if excess of sodium or potassium bicarbonate is added to a solution of any salt of cobalt, and then hydrogen peroxide, a green liquid is formed.

This liquid appears to contain a cobaltate or cobaltic acid, H_2CoO_4 , for, although the substance has not at present been isolated, volumetric determinations show that the maximum green colour is reached when the molecular proportions of the cobalt salt and hydrogen peroxide are as 1 : 2; a probable reaction is—



The green solution may be formed in presence of nickel salts, and the reaction serves as a ready method both of detecting cobalt, even in presence of large excess of

nickel, and of detecting nickel in presence of considerable excess of cobalt.

*53. "*Ethereal Salts of optically active Malic and Lactic Acids.*" By THOMAS PURDIE, F.R.S., and SIDNEY WILLIAMSON, Ph.D.

J. Wallace Walker (*Trans.*, 1895, lxvii., 914) has shown that the rotations of the ethereal salts of active lactic acid are much greater when prepared by the action of alkyl iodide on silver lactate than by the direct action of acid on alcohol in presence of a mineral acid. To see if the same holds good in the cases of the other oxy-acids, the authors have prepared the ethereal salts of malic acid through the silver salt, and have compared the rotations of the salts thus obtained with the rotations of the same salts prepared from the alcohol. In every case the salts prepared from the silver salt were found to have the higher rotation.

The same result was evident on comparing the rotation of ethylic lactate prepared by the different methods. On the other hand, ethylic acetylmalates, prepared by the two methods, were found to have nearly the same rotation. A similar result was observed in the case of ethylic acetylactate.

The ethereal salts of both malic and lactic acids prepared from the alcohols were examined for racemoid compounds, but the quantity found was not sufficient to account for the low activity; this, coupled with the fact of the constancy of the activity of the ethereal salts prepared with the aid of mineral acids by various observers, and the similarity in rotation of the acidyl compounds from ethers from both sources, lead the authors to think that some other explanation of the difference of activity of the ethereal salts prepared by the two methods must be found than the supposition that the mineral acids cause racemisation.

In examining dextro-ethylic chloropropionate prepared from lævo-ethylic lactate for the presence of racemised salt by converting it into zinc lactate, it was found that the optical activity of the recovered salt was opposite to that of the zinc lactate from which the chloropropionate was derived. The active lactic acid had undergone inversion by the action of phosphorus pentachloride, as Walden (*Ber.*, 1896, xxix., 133) has recently noticed in the case of the malic acids.

54. "*Metadichlorobenzene.*" By FREDERICK D. CHATTAWAY and R. C. T. EVANS.

Metadichlorobenzene, although well known, is extremely costly and difficult to procure, and no directions for preparing it in quantity are available. The authors, having required large quantities of this compound for an investigation of some derivatives of benzene, have worked out a simple and very satisfactory method for obtaining it easily in bulk.

Acetanilide, dissolved in hot acetic acid, is treated with a thin paste of bleaching powder until two hydrogen atoms, occupying the meta-positions with respect to one another, are replaced successively by chlorine and a heavy liquid addition product of hypochlorous acid, and the 1:3:4-dichloroacetanilide is formed. On cooling, this sinks, is readily separated, and when treated with hot alcohol rapidly decomposes, 1:3:4-dichloroacetanilide crystallising out. The dichloroacetanilide is then heated with strong sulphuric acid, which hydrolyses it, and on pouring the solution over ice 1:3:4-dichloroaniline separates. The dichloroaniline, dissolved in a large quantity of alcohol, is then mixed with an excess of hydrochloric acid and diazotised by sodium nitrite, when, as the temperature rises from the reaction, the diazo-group first formed is replaced by hydrogen.

The yield of 1:3:4-dichloroaniline is nearly quantitative, and that of the metadichlorobenzene over 50 per cent of the weight of acetanilide taken.

55. "*On the Temperature of certain Flames.*" By W. N. HARTLEY, F.R.S.

The author, having for many years past studied the

nature of flames and the spectra they emit, found no practicable means of measuring their temperature, owing to the disproportionate size of the measuring instrument (a thermo-electric couple for instance), compared with the effective volume of the flame. He measured the temperature of flames by means of gold-leaf and with fine wires of platinum 1/3000 in. diameter, such as were drawn by Wollaston and used by Faraday, also with pure platinum wire 1/1000 in. thick. He furnishes evidence of the high temperature of a candle-flame, not only from the melting of gold and of platinum in the flame, but by an examination of the spectrum to be seen in the mantle. Experiments made with platinum wires heated in a bat's-wing gas flame are described, which proved that the carbon does not lower the melting-point of the platinum, at any rate in any appreciable degree. A small carbon monoxide flame melts platinum wire 1/1000 in. in thickness, and a cyanogen flame was shown to be intensely hot, for it melted such wire with extreme ease. The author believes that his experiments have dissipated the doubt that was cast on Professor Smithells' statement of the high temperature of the mantle of the Bunsen flame, and confirm his own estimate of the high temperature of the Bessemer flame.

56. "*The Determination of the Composition of a White Son by a method of Spectrographic Analysis.*" By W. N. HARTLEY, F.R.S.

It is not long since, among current coin in France, there were sous of a peculiar golden-yellow colour, which were termed "white." It was supposed that they were made during the French Revolution of 1798 from any metal which could be readily appropriated, and great doubt expressed as to their composition.

To analyse the coin without injury, the method of photographing its spectrum was resorted to. The metals present being first ascertained, their relative proportions were subsequently arrived at by comparing the photograph with a series of quantitative spectra, in which solutions of known strengths yield spectra with a certain number of lines of definite length and strength. When the composition of the coin within certain limits had been thus ascertained, alloys were made to imitate the metal, and photographs of these were taken.

The third trial produced an alloy, the spark spectrum of which yielded a photograph identical with that of the coin, and its composition was found by the usual methods of analysis to be—

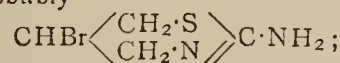
Lead	13.93 per cent.
Copper	72.35 "
Iron	0.85 "
Zinc	12.70 "
	<hr/>
	99.83

The alloy is thus seen to be a kind of brass, in which lead takes the place of about one-half the zinc. It is also richer in copper. The coin does not ring, and its edges show signs of being cracked, which may be readily accounted for by the large proportion of lead which enters into its composition.

By the method of analysis here described, it may be advantageous and interesting to determine the composition of antique jewellery and coins, as no injury results from the action of the spark.

57. "*Halogen additive Products of substituted Thiosinnamines.*" By AUGUSTUS E. DIXON, M.D.

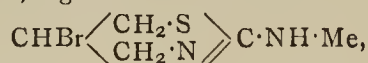
It has been recently shown by the author (*Trans.*, 1896, lxi., 17) that the "thiosinnamine dibromide" obtained by Maly (*Zeit. f. Chem.*, 1867, 42) from bromine and allylthiourea is the hydrobromide of a penthiazoline derivative, probably—



and is, moreover, identical with the substance produced by combining dibromopropylthiocarbimide with ammonia.

This thiocarbimide unites readily with primary and secondary amines, yielding analogous compounds. The author has lately been engaged in experiments on the production of these compounds from bromine and substituted allylic thiocarbamides. Only the phenyl and orthotolyl derivatives had been tried, the former unsuccessfully, when an abstract appeared, in the last issue of the Society's Journal, of a paper by Gadamer (*Arch. Pharm.*, cccxxiii., 646), showing that the addition compounds can be satisfactorily obtained from substituted allylic thiocarbamides (thiosinamines) containing fatty (methyl) groups.

An examination of Gadamer's "methylallylthiocarbamide dibromide," $C_5H_{10}N_2SBr_2$, shows it to be saline in nature; it is, in fact, the hydrobromide of a base ($C_5H_9N_2SBr$), which is liberated on treatment of the aqueous solution with dilute alkali. The same compound, $C_5H_9N_2SBr \cdot HBr$, is formed by mixing alcoholic solutions of dibromopropylthiocarbimide and methylamine; the author, therefore, on the grounds set forth in the paper first mentioned, regards the base as—

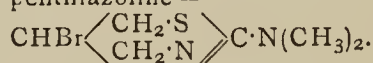


μ -methyl- γ -brompenthiazoline.

By analogy, it is suggested that the dimethylallylthiocarbamide dibromide, obtained by Gadamer from—



and bromine, is probably also the hydrobromide of a dimethylated penthiazoline—

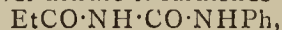


58. "Acidic Thiocarbimides, Thioureas, and Ureas." By AUGUSTUS E. DIXON, M.D.

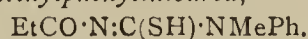
The method of preparing acidylthiocarbimides by heating the corresponding acid chlorides, dissolved in anhydrous benzene, with lead thiocyanate (Dixon and Doran, *Trans.*, 1895, 565; Dixon, *ibid.*, 1040), has now been applied to the chlorides of propionic, isobutyric, and phenylacetic acids, the yields of dissolved thiocarbimide so obtained varying from 90 per cent of the theoretical to a nearly quantitative amount. The products are pale yellowish in colour, have a characteristic, pungent, and tear-exciting odour, and are decomposed by heating with water, with formation of thiocyanic acid; they give the ordinary thiocarbimidic reaction (desulphurisation) when warmed with ammoniacal silver or alkaline lead solution, and unite spontaneously with primary and secondary amines, yielding acid substituted thiocarbamides or thioureas; the former dissolve readily in dilute caustic alkali, exchanging the acid radicle for hydrogen. When treated in boiling alcoholic solution with silver nitrate, they exchange sulphur for oxygen, thereby affording the corresponding (acidic) ureas.

The following substances are described:—

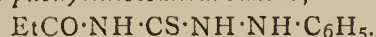
ab-Propionylphenylthiocarbamide, $EtCO \cdot NH \cdot CS \cdot NHPh$.—Brilliant, colourless prisms, m. p. 129—130°, undecomposed. With silver nitrate it furnishes—



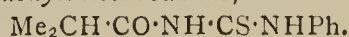
identical with the compound obtained by Kühn (*Ber.*, xvii., 2881) from phenylisocyanate and propionamide. ab-Propionylorthotolylthiocarbamide.—Hair-like needles, m. p. 143—144°. ab-Propionylmetatolylthiocarbamide.—Long, vitreous prisms, m. p. 86—87°. ab-Propionylparatolylthiocarbamide.—White needles, m. p. 127.5—128.5°. n-Propionyl- ν methylphenylthiourea,—



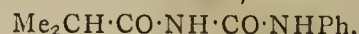
Large, vitreous prisms, m. p. 68—69°. n-Propionyl- ν -phenylbenzylthiourea.—Thick prisms, m. p. 102—103°. a-Propionyl- β -phenylthiosemicarbazide,—



Obtained from propionylthiocarbimide and phenylhydrazine; tufts of brilliant white prisms, m. p. 155—156°. ab-Isobutyrylphenylthiocarbamide,—

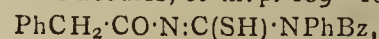


—Large, colourless prisms, m. p. 128.5—129.5°. With silver nitrate it affords the urea,—



identical with that obtained by Pinner (*Imidoäther*, 124, from butenyldiphenyldiureide and acetic acid. ab-Isobutyrylorthotolylthiocarbamide.—Short, white needles, m. p. 136—137°. The urea, $Me_2CH \cdot CO \cdot NH \cdot CO \cdot NH \cdot OTo$, forms long, flexible, satiny needles, melting at 134—135°. ab-Isobutyrylparatolylthiocarbamide.—Large, ice-like prisms, m. p. 134—135°. The urea crystallises from alcohol in shining needles, melting at 137—138°. ab-Isobutyrylalphanaphthylthiocarbamide.—Fine needles, m. p. 167.5—168.5°.

Phenacetylthiocarbimide, $PhCH_2 \cdot CO \cdot NCS$, has a feeble odour, and attacks the eyes only slightly. By combination with aniline it affords $PhCH_2 \cdot CO \cdot NH \cdot CS \cdot NHPh$. ab-Phenacetylphenylthiocarbamide.—Lustrous, white prisms, m. p. 109—110°. The corresponding urea forms thin, white needles, melting at 168—169°. ab-Phenacetylorthotolylthiocarbamide.—Vitreous prisms, m. p. 149—150°. With nitrate of silver it gives the urea; silky, flexible needles, m. p. 161.5—162°. ab-Phenacetylparatolylthiocarbamide crystallises from alcohol in brilliant, rhombic plates, melting at 150—151°. The urea occurs in hair-like needles, of m. p. 189—189.5°.—



n-Phenacetyl- ν -phenylbenzylthiourea.—Microscopic prisms, m. p. 127.5—128.5°.

All the compounds enumerated above are insoluble, or nearly so, in water; the disubstituted thiocarbamides are all desulphurised by warming with alkaline lead tartrate, or by ammoniacal silver nitrate in the cold; the trisubstitution derivatives, on the contrary, do not give up their sulphur under these conditions.

Attempts made to obtain from picryl chloride, using either lead or mercuric thiocyanate, the corresponding picrylthiocarbimide, $C_6H_2(NO_2)_3 \cdot NCS$ were unsuccessful. Experiments on the chlorides of phenylsulphonic and ethylsulphuric acids are now in progress.

59. "Apparatus for the Detection of Boric Acid." By W. M. DOHERTY, Government Laboratory, New South Wales.

The milk, wine, or other substance is made slightly alkaline with sodium carbonate, and after drying, it is thoroughly charred, not burned to an ash. The charred mass is extracted with boiling water, and the solution obtained made acid with hydrochloric acid, and evaporated gently over the water-bath in a small porcelain boat, which is placed in an apparatus of the following description:—

A piece of glass tubing, about 9 inches long and $\frac{1}{4}$ inch in diameter, is turned over at right-angles at one end and drawn to a fine aperture. A second piece of tubing about 2 $\frac{1}{2}$ inches long and $\frac{1}{4}$ inch in bore is provided with a hole in the side, and placed over the aperture and arranged so as to form a glass Bunsen burner.

The porcelain boat or other vessel containing the properly prepared substance, supposed to contain the boric acid, is placed in the larger tube, which is attached at the wide end to the gas supply, the whole being supported by a clamp. The gas is regulated so as to produce a clear flame about $\frac{1}{2}$ inch long, and free from luminosity at the extremity of the upright tube. The vicinity of the porcelain boat is heated by an ordinary Bunsen burner, and if boric acid be present, even in the most minute quantity, the small flame will show it distinctly. It will be found desirable to apply the heat gently, increasing it slowly, and carefully observing the flame in the meantime.

Lothar Meyer Memorial Lecture.

The Lothar Meyer Memorial Lecture will be delivered by Professor P. Phillips Bedson, D.Sc., at an extra meeting of the Society, on Thursday, May 28, at 8 p.m.

NOTICES OF BOOKS.

The True Atomic Weights of the Chemical Elements and the Unity of Matter. By GUSTAVUS DETLEF HINRICHS, M.D., LL.D. St. Louis, Mo., U.S.: Carl Gustav Hinrichs. New York: B. Westermann and Co.

THE key to the whole of this remarkable book is to be found in a sentence quoted on page 54 by the author, as having been used by him in a conversation with his Professor, in his early student days:—"It must be possible! It ought to be made possible!"

The apparent object of the book is to show that the atomic weights of the elements are exact multiples of half the atomic weight of hydrogen, or of a common substance which he calls "pantogen," and that the work of chemists on this subject for the past fifty years, and in particular the work of Stas, is to be summed up as "rubbish of a spurious accuracy and imaginary analysis."

The book is divided into three parts. Part I. deals with the present system of atomic weights, or, as it is termed, "The School of Stas."

Part II. is chiefly occupied with an exposition of the author's "limit method" of determining the exact atomic weights.

Part III. professes to deal with the composition of the chemical elements and the unity of matter.

We propose to consider in detail some of the points brought forward; but, before doing so, think it would be well to touch a little upon the general character of the work as a whole,—and "right here," to use one of the author's favourite expressions, we must say that for absence of the commonest courtesy to men who are deservedly recognised as leaders in chemistry, we have never seen the like!

The author, in his desire to *make* his theory possible, sets to work to tear down and trample upon the work of all those chemists whose researches point to the conclusion that the true atomic weights of the elements cannot be referred to half atoms of hydrogen. The work of Stas appears to particularly irritate the author, probably because of the very thorough manner in which it was carried out, and it comes in for an amount of abuse that is really amusing when one considers the relative values of the two men deduced from the work that they have done! Unfortunately Stas is dead; but if he were alive his criticism of Prof. Hinrichs would be lively reading. As for the part that Lothar Meyer and Mendeleeff have taken in the periodic classification of the elements, the former is accused of plagiarism and the latter of vain vapourism. It is in this spirit that the author makes a *cool* critical examination of the progress of chemistry for the past fifty years!

In Part II. the work of Dumas is considered with especial reference to the determination of the atomic weight of carbon by the combustion of the diamond, and it is here "insisted" that Stas was nothing but assistant to Dumas in that research, and had no part in the real scientific work accomplished by Dumas. How this information is arrived at is not very clear, especially when it is recorded a few pages further on that Dumas included the name of Stas in the title of this very research! But granting for the moment that it was so, what better schooling could he have had, and what could better have fitted him for the work to which he devoted his life? On page 30 the special characteristic of Stas's determinations of atomic weights in the use of large quantities of material is touched upon, and the author appears to regard the object of this method as being simply to *impress* the chemical world with Stas's extraordinary manipulative skill, and he appears to be unable to see that the real object that Stas had in view was to get nearer to the truth.

In the fact that in 1865 Stas gave as the value for nitrogen 14.044, and then after seventeen years' work he

was able to give—in 1882—as a closer approximation the figures $N = 14.055$, the author can see nothing but what he is pleased to call "sleight of hand." Following Stas, Ostwald, Clark, Stebeleen, Van der Plaats, Thomsen, and Lothar Meyer, each come in for a full share of criticism (?) of the same order, apparently because they are unable to accept the hypothesis of Prout as consistent with experimental fact.

We next come to a "critical examination of Stas." We only purpose to select one example, and leave our readers to judge from it the value of the remainder. Stas, in his synthesis of silver nitrate, gives two values—one for the "dried" and another for the "fused" nitrate. On page 86 a quotation is given from a private letter sent by Stas to Van der Plaats, in which Stas states that the dried salt is the true nitrate, because "by fusion a slight decomposition takes place." On the very next page the author affirms that "The only legitimate conclusion that can be drawn from these experiments is that chemical compounds do not contain the elements in fixed proportions; for the amount of silver nitrate from a given weight of silver varies continuously and regularly with the absolute weight of silver employed, . . . and is constantly larger for the dried nitrate than for the same chemical compound when it has been fused."

Part II. introduces the limit method for determining the true atomic weights. Starting with the assumption that the atomic weight of every element must be a simple multiple of half the atomic weight of hydrogen, the author evidently selects the table of latest determinations and sweeps away all departures from round numbers as "spurious accuracy," so arriving at what he calls the common atomic weights of the elements. Taking this series as standard, he tabulates the results of various observers, Stas in particular, and finds that in a general way, as the quantity of material used in each individual experiment increases, the departure from the common atomic weight also increases, and that the departure from unity— H being taken as 2—is as the sum of the weights of material used in the determinations.

In this truly original manner the conclusion is arrived at that the determination of the dissociation of potassium chlorate by Penny, in 1839, who operated upon 5 grms. of material, is nearer to the truth than that of Stas, in 1860, who used 100 grms.¹ Hence to determine the *true* atomic weight of any element, all that is required is to make a series of determinations under the same conditions, using the same materials, differing only in the amount taken, plot the results in a curve having as abscissa the weights of material taken and the analytical ratio as ordinates, then continue the curve so as to cut the ordinate axis,—and this point will be the true atomic ratio. It seems delightfully simple, but the whole theory rests upon the assumption that the only effect of increasing the weight of material used in a determination is to recede from the true value by the introduction of foreign matter—an assumption that is scarcely likely to be generally admitted.

The author seems to feel the weakness of the situation, and on page 183 we note a very ingenious attempt to introduce Dumas as a kind of support. A quotation from the work of that illustrious *savant*, on the Dissociation of Iceland Spar, is given. "To verify their accuracy (the atomic weights) . . . we must make analysis or synthesis on a large scale." "If," says Prof. Hinrichs, "instead of 'large scale' we say a *series* of increasing amounts of matter, this word of Dumas may be taken to-day as the safest guide to obtain the true atomic weights."

In Chapter III., "A Rational System of Atomic Weights," the author considers that as a standard of matter both gases and liquids are inadmissible, and proposes to reject H or O , and to take carbon in the form of diamond with an at. wt. = 12 as a standard, and as a unit exactly one-twelfth of this.

The work of Dumas is again quoted in connection with

the atomic weights of oxygen, hydrogen, and calcium, and, after the application of the favourite method of sweeping away all small departures, these elements are expressed as whole numbers.

In Part III., following this chapter, Mr. Hinrichs gives some interesting modern alchemy on the question of the possibility of the transmutation of lead and tin into gold. A rather startling piece of logic is found here. As it was held impossible to produce artificially the crystalline form of carbon known as diamond, and this supposed impossibility has now been proved to be fallacious, nothing should be looked upon as impossible, even to the manufacture of gold from the proper quantities of lead and tin! And the prediction is made that, in the hands of a Moissan of the twentieth century, "the autoclave charged with base metals may yield pure gold."

It is scarcely worth while to follow the author much further. In fact Vol. I. properly ends here, the Supplement which follows deals with the classification of the elements and a sketch of the Periodic Law. This is said to have been introduced by Lothar Meyer and Mendeleeff, and it is said of it that "so far as it was new it is not true, and so far as it is true it was not new." It is intimated that Lothar Meyer really got the idea from one of the author's papers, and then published it as his own. Mendeleeff is severely handled, chiefly on account of his predictions of elements; his periodic classification of the elements is given on page 246, and each class is taken in detail, and the mistakes and errors explained in choice language. As an example, Row 9 is said to be "indeed a chimera, the vain vapouring of an empty empiric brain."

The book now concludes with a kind of dramatic sketch, in which the possessor of truth—presumably the author—poses as a victim who is struck down and robbed by a highwayman, who, after having silenced him as he supposed for ever, publishes as his own as much of his victim's book as his "limited capacity can comprehend" under the high-sounding title of "The Periodic Law."

We have gone much more fully into this work than we should have done had not the author taken the trouble to suggest to us that our criticism, published some years ago, of his "Programme of Atom Mechanics," was written without our having read the work. In the present case, as in the former, although a few quotations here and there would have been amply sufficient, we have gone carefully through the book, and we must confess that the task was not a pleasant one. In reviewing the work of chemists for the past fifty years there are undoubtedly many instances to be found of faulty observations, hasty conclusions, and accidental errors. No man's work is perfect, and it is only by the painstaking elimination of errors discovered by experimental work that we can hope to get nearer to the goal of all true investigators, TRUTH. It would be well if at least those who occupy the position of teachers would keep this in mind, for it has been well said, by one of our most successful physicists, "There can be no great harm in a student taking an erroneous view; but when great minds err, the world must pay dearly for their mistakes."

The grand hypothesis of the unity of matter is coming more and more prominently before us every year, but we believe that that truth will be demonstrated by patient and laborious work in the laboratory, gaining here a little and there a little; work such as the classical researches of Stas furnish a luminous example. Normally, truth is gained as the result of experiment, and we cannot too strongly denounce the system that first conceives an idea, and then sets to work to *make* experimental data agree with it. We have faith in the unity of matter, but we believe also that the demonstration of it is more likely to be found in the work of the painstaking *follower* of true research than upon the "black walnut blackboard one metre square" that has been in use by the author of "Atom Mechanics" for nearly thirty years.

CORRESPONDENCE.

THE RÖNTGEN RAYS.

To the Editor of the Chemical News.

SIR,—With reference to the "Action of X Rays upon Electrified Bodies" (CHEM. NEWS, vol. lxxiii., p. 211), I have found in every case that, immediately the tube is excited, the gold leaves of the electroscope at once diverge, touch the sides, collapse, diverge again, and so on, as long as the tube is at work. The charge seems to be negative. While upon the subject of X rays, as I have seen no mention of the following fact I should like to suggest that, in the use of fluorescent screens of potassium platinocyanide, it is a great advantage to add a small quantity of calcium chloride. The addition of a deliquescent salt keeps the fluorescent material in a condition best suited to good results.—I am, &c.,

F. I. REID.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 16, April 20, 1896.

Extraction of the Terpenic Alcohols contained in Essential Oils.—A. Haller.—The recent publication by Tiemann and Krieger on a "Method of Purifying Alcohols," specially applied to the alcohols contained in essences, compels us to make known the researches which we have for some time been conducting in the same direction. In our study on the borneols, and in particular on the camphor of rosemary, we have since 1889 utilised the property of bibasic acids for yielding with alcohols acid ethers, soluble and saponifiable by alkalis, for separating borneol from camphor. Our researches apply to different varieties of essences of geranium and citronella, of American mint, and of spike.

The Diffraction of Röntgen's Rays.—L. Calmette and G. T. L'Huillier.—Already inserted.

Observations on a Communication by MM. Benoist and Hermuzescu.—Auguste Righi.

Photography in the Interior of the Crookes Tube.—G. de Metz.—The author has obtained a dozen photographs. It seems that the cathodic rays in the interior of the Crookes tube have one of the properties of the Röntgen rays, since they penetrate aluminium, pasteboard, sensitive paper, and films, but they are stopped by platinum (0.32 m.m.) and copper (1.26 m.m.). M. Poincaré added some observations questioning that the cathodic rays possess the essential properties of the Röntgen rays.

Rotatory Dispersion of Liquids, not Polymerised.—Ph. A. Guye and Ch. Jordan.—The author concludes that—1. Active liquids, not polymerised, present only the phenomenon of normal rotatory dispersion. 2. The coefficient of dispersion in the violet, being arranged according to increasing values, it is not the same for all the other coefficients; each active body follows its own especial law of rotatory dispersion. 3. The usual rotatory powers $[\alpha]_D$ being arranged in their absolutely increasing values, the coefficients of dispersion in the violet have no—even approximate—proportionality with the rotatory powers. 4. The specific rotatory dispersions, without being proportional to the rotatory powers $[\alpha]_D$, nevertheless increase generally at the same time as the latter, the bodies with a strong rotatory power having a strong specific dispersion, and inversely; the specific dispersions are nevertheless sometimes greater and sometimes smaller

than the usual rotatory powers; the specific dispersion is therefore a constant characteristic of a chemical compound as well as the usual rotatory power. 5. There is no simple relation between the refrangibility of different radiations and the rotatory dispersions.

New Series of Sulphophosphides.—M. Ferrand.—The author has obtained, by Friedel's method, a second series of sulphophosphides, the thiopyrophosphates, P_2S , M'_4 , i.e., those of copper, iron, silver, nickel, chromium, zinc, cadmium, mercury, lead, and aluminium.

Influence of Induction Currents on the Orientation of Living Bacteria.—L. Lorlet.—Living bacteria, in the state of motile bacilli, are very sensitive to the influence of induction currents, and arrange themselves immediately in the direction of the current. As soon as an antiseptic liquid has rendered them motionless, or has caused them to perish, the influence of electricity is annulled.

MISCELLANEOUS.

Action of the Cyanacetates of Sodid Propyl, Butyl, and Amyl upon Diazobenzene Chloride.—G. Favrel. The cyanacetates of propyl, butyl, and amyl are apt, like their lower homologues, to form hydrazones or azo-derivatives by reacting on the diazobenzene chloride, and to produce, like to them, two isomeric modifications. — *Comptes Rendus*, cxxii., No. 15.

Detection of Argon in Gases issuing from the Earth.—R. Nasini and F. Anderlini.—In the gases which issue in abundance from the hot springs of Abano, and which contain CO_2 10 per cent, H_2S 1.13 per cent, CH_4 12 per cent, and N 75.7 per cent, the authors could not detect any quantity of argon worth mention. — *Gazzetta Chimica*.

Facts concerning Argon.—R. Nasini and F. Anderlini.—The authors, in their endeavour to trace atmospheric argon to the origin which they suggested in the first place in nitrogenous gases escaping from the interior of the earth, have also attempted to separate argon from the air. In so doing they have always found decidedly less in the gaseous residue not absorbed by magnesium than Lord Rayleigh and Prof. Ramsay. They observed that when the gaseous residues were passed over a fresh portion of magnesium a further portion of the gases was absorbed. Further, the noteworthy fact was observed that such gaseous residues first yielded in Geissler tubes the nitrogen spectrum, which then passed into the brilliant spectrum of argon. But after a longer or shorter time this always again disappeared and gave place anew to the nitrogen spectrum. But soon this also ceased, and at the same time the passage of the discharge through the Geissler tube. This phenomenon was observed quite invariably in all the specimens examined, showing that the argon under the influence of heat is in some manner absorbed in the Geissler tubes. — *Gazzetta Chimica* and *Berichte*.

MEETINGS FOR THE WEEK.

- MONDAY, 18th.—Society of Arts, 8. (Cantor Lectures). "Applied Electro-Chemistry," by James Swinburne.
— Medical, 8.30. (Annual Oration).
TUESDAY, 19th.—Royal Institution, 3. "Ripples in Air and on Water," by C. V. Boys, F.R.S.
— Institute of Civil Engineers, 8.
— Photographic, 8.
— Pathological, 8.30. (Anniversary).
— Society of Arts, 8. "Bronze Casting in Europe," by George Simonds.
WEDNESDAY, 20th.—Society of Arts, 8. "Orthochromatic Photography," by Capt. W. de W. Abney, F.R.S.
— Meteorological, 7.30.
— Microscopical, 8.
THURSDAY, 21st.—Royal, 4.30.
— Royal Society Club, 6.30.
— Royal Institution, 3. "The Art of Working Metals in Japan," by W. Gowland F.C.S.

Chemical, 8. "The Diphenylbenzenes—I. Metadiphenylbenzene," by F. D. Chattaway, M.A., and R. C. T. Evans. "Derivatives of Camphoric Acid," by Dr. F. S. Kipping. "Some Substances exhibiting Rotatory Power both in the Liquid and Crystalline States," by W. J. Pohes.

FRIDAY, 22nd.—Royal Institution, 9. "Hysteresis," by Prof. J. A. Ewing, F.R.S.

— Physical, 5. "On Dielectrics," by R. Appleyard. "The Field of an Elliptical Current," by J. Viriamu Jones. "An Instrument to Measure Frequency," by A. Campbell.

SATURDAY, 23rd.—Royal Institution, 3. "Three Emotional Composers—III. Liszt," by F. Corder, Curator, Royal Academy of Music.

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C. J. STEWART, Clerk of the Council.

Spring Gardens, S.W.,
9th May, 1896.

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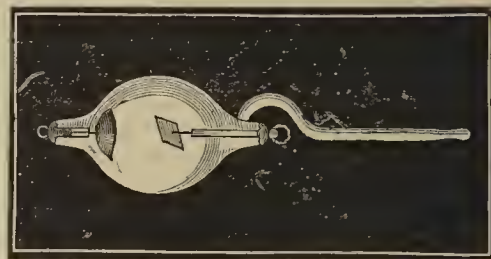
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THE CHEMICAL NEWS.

VOL. LXXIII, No. 1904.

A NEW KIND OF RAYS.

ACCORDING to Röntgen's most recent communications in the *Transactions of the Würzburg Physical Society*, the X rays are able to discharge electrified bodies exposed to the air; the discharge ensuing the more rapidly the more intense the rays. Hereby, it is in general indifferent whether the electric substances are conductors or non-conductors. In an electrified conductor surrounded with a solid insulator, e.g., paraffin, the effect of the irradiation is the same as on stroking this insulating coating with a flame conducted off to the earth. But if the insulating coating is surrounded with a tightly-fitting conductor connected with the earth, and pervious to the X rays, no effect of the X rays can be shown upon the inner electrified substance. The discharge of electrified bodies which are not touched themselves by the X rays can be effected also by air irradiated by the X rays. A brief contact of the air with a body of a large surface is sufficient to annul the property communicated to the air by the X rays. The discharge of electrified bodies by the X rays takes place also in an atmosphere of hydrogen. In tubes highly exhausted, the discharge of a substance which has been directly exposed to the X rays is much slower than in vessels filled with air or hydrogen at the ordinary pressure. In many cases it is advantageous to interpolate between the discharging apparatus furnishing the X rays and the Ruhmkorff spark inductor, a Tesla transformer, as the discharging apparatus is not so readily perforated, and many apparatus yield more intense X rays. As regards the investigation on the origin of the rays, it appears that all solid bodies are capable of yielding X rays under the influence of the cathodic rays; among metals, platinum is the one with which we can obtain the most intense rays. Latterly, Röntgen employs a discharging apparatus in which the cathode is a concave mirror of aluminium, and the anode is a sheet of platinum placed in the centre of the curvature and inclined at an angle of 45° towards the axis of the mirror. In this apparatus the X rays emanate from the anode. The intensity of the rays is perfectly independent of their production from the anode or the cathode. — *Chemiker Zeitung*.

ON THE FUSIBILITY OF PLATINUM IN A CARBON BLAST FURNACE.

By VICTOR MEYER.

In a memoir from the pen of a thorough expert it has been recently pointed out that the oft-repeated assertion of the fusibility of platinum in a furnace fed with carbon and air has not been incontrovertibly demonstrated. As the vessels used are in general more or less injured at the high temperature of the experiment, or cannot be considered as perfectly fitting, it is not impossible that the flames of the furnace or burning particles of carbon may come in direct contact with the platinum. But, as is well known, in almost every flame there is a hot region having a higher temperature than the melting-point of platinum. A capillary platinum wire can be fused in the hottest part of the flame of a candle. The problem of fusing platinum in the carbon blast furnace in vessels perfectly closed on all sides does not seem to have been hitherto solved in a manner which excludes all doubt.

In the course of the pyro-chemical investigations which for some time have engaged me, in concert with Dr. von Rocklingshausen and Dr. Locke, we have undertaken the task, among other things, of obtaining a fire-box in which platinum can be fused, whilst an alloy of 25 per cent iridium and 75 per cent platinum remains unattacked. We needed such a fire-box for determinations of the density of gases and measurements of temperature, which are undertaken with the apparatus made for us by Hæraeus, of platinum-iridium.

For this purpose we used a furnace quite similar to the blast furnace used by C. Langer and myself, though of larger dimensions, and especially provided with a much larger wind-chest. As fuel we used retort-graphite, broken up in pieces of the size of a hazel-nut. The air was supplied by a very powerful blast. Under certain conditions this furnace answers the purpose required, as is proved by the following experiment:—

We formed a block of perfectly refractory earth in which were two depressions, so that it might be regarded as a double crucible with very thick sides. In one of these depressions was laid a piece of sheet platinum, and in the other a sheet of metal of equal size of the alloy of 25 parts iridium and 75 platinum, which we had previously proved to be considerably less fusible than platinum. The block was then perfectly closed by means of a top of the same refractory earth, so that the whole formed a massive stone-like mass with two cavities.

On burning, the crucible thus formed was converted into a stone perfectly solid and hard. After it had been heated in the above graphite blast furnace, and allowed to cool, it was broken open. The platinum was melted into a ball, but the platinum-iridium alloy was perfectly unaffected.

Hence we must add to the above-quoted remark of H. Hecht the supplement, that now the fusibility of platinum in thick-sided crucibles with a carbon blast furnace is indubitably established. The metal had neither been contaminated with particles of carbon nor by any constituents of the crucible. The platinum-iridium alloy had retained its outer form and its lustre quite unaltered. The admission of furnace gases had been obviated in our experiment much more perfectly than with any previous arrangement of apparatus.

ARGON AND HELIUM IN THE SYSTEM OF THE ELEMENTS.

By W. PREYER.

WHAT places in the system of the elements must be assigned to the indifferent gases argon and helium, as well as to the element discovered by Runge and Paschen in the gases obtained from clèveite (having a lower molecular weight than helium), and not yet named, is a far-reaching question. On the reply, it may depend whether an attempt to represent certain properties of the elements as periodic functions of the atomic weights has a prospect of success. As long as a fixed place in the system has not been allotted to every single known element, all attempts to ascertain the nature of these functions are premature, since we must first establish how many and what elements constitute a period.

Hitherto, in the series from hydrogen to uranium, arranged according to the atomic weights, no single period has met with universal recognition. No one denies that periods exist, but we can no longer—as before the discovery of the two gases with the atomic weights 4 (He) and 20 (Ar)—accept as given the five periods, i.e., lithium—fluorine, sodium—chlorine, potassium—manganese, copper—bromine, silver—iodine, in addition to the fact that iron, nickel, and cobalt, and the platinum metals, as also the metals of the rare earths, in all projects disturbed the assumed and desired symmetry.

In addition, we have the necessity of placing tellurium, not before, but after iodine; since, according to the most trustworthy determinations (both of Brauner and of Standenmair) it has an atomic weight of from 127.6 to

same solution of zinc chloride, in which ordinary silk is at once dissolved on slight heating, does not entirely dissolve tussah silk, even on prolonged boiling. We have further to notice the behaviour of tussah silk on combus-

±	+	+	+	±	-	-	-	±	±	±	+	+	+	±	-	-	-	±
He	Li	Be	Bo	C	N	O	Fl	As	21	22	Na	Mg	Al	Si	P	S	Cl	37
38	Ka	Ca	Sc	Ti	Va	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br	82
83	Rb	Sr	Yt	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	—	I	Te
130	Cs	Ba	La	Ce	Nd	Pr	—	—	Sm	—	—	Gd?	—	Tb	—	Er	—	Dp?
Yb	—	—	—	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—	217
—	—	—	—	Th	—	U	—	—	—	—	—	—	—	—	—	—	—	—
	I.	II.	III.	IV.	III.	II.	I.				I.	II.	III.	IV.	III.	II.	I.	

127.7. Its specific heat points in the same direction. An element, 125, with a rather higher specific heat than tellurium and more strongly electro-negative, has yet to be discovered.

If, now, in order to meet these new requirements, without shaking the established relational affinities of the elements, we for the present regard, in the quest for the natural periods, exclusively their electro-chemical behaviour and their valence, the electro-positive, the electro-negative, and the electrically indifferent elements must be placed together according to their ascending atomic weight. The accompanying table shows the result when hydrogen and the new, not as yet named, gas are placed first.

The slightest and most fluctuating electro-chemical tension is found in the elements of the helium line, of the C and Sr line, and the triple argon-platinum line, and of the triple line to the right in which tellurium has its place.

The Roman characters show the valence of the elements placed above. Where they are absent the valence is still uncertain and may be smaller than 1.

The atomic heat increases in every vertical column from above downwards.

The evidence for these and other systematic relations is found in the author's work ("Das genetische System der Chemischen Elemente," Berlin, Friedlander, 1893). The table is there lithographed. I have here added three elements subsequently discovered, and the new elements thereby postulated, which, like all the ± elements not belonging to the carbon-silicon stem, lie quite near to the axis of the abscissæ.

In this graphic representation, as shown in the above table, the periodicity appears so distinctly that mathematical speculation might already take up the question of what kind may be the dependence of the properties of the elements (quantitatively determinable) on their atomic weight.—*Berichte*, xxix., p. 1040.

RECOGNITION OF TUSSAH SILK IN TEXTILE GOODS.

By Dr. F. FILSINGER.

TUSSAH silk is distinguished microscopically from true silk (that secreted and spun by the larva of *Bombyx mori*) in that the cocoon thread has a flatter section and a greater breadth; it contains numerous fine air-channels running axially, and numerous intersections, generally placed obliquely. Still more significant is the chemical behaviour of the tussah silk. It is well known that the basic solution of zinc chloride, the alkaline solution of copper glyceride, and concentrated hydrochloric acid, dissolve the silk of *Bombyx mori* easily and completely. On the other hand, tussah silk resists these reagents so persistently that they are slowly and imperfectly dissolved, leaving behind a stratum of sericin which merely swells up, so as to convey the impression of insolubility. The

tion, and the odour given off. If we approximate some twisted-up threads of ordinary silk to a flame, so that it merely touches the ends, they are certainly kindled; but the silk does not go on burning, and forms a globular coalescent mass, giving off the intense and characteristic odour of burning horn and hair. Tussah silk burns much more vividly, probably in consequence of the numerous air-channels; it glows on like cotton, and emits little of the odour of highly nitrogenous substances. Of course for these tests the specimen must be prepared by treatment with dilute hydrochloric acid, and careful washing to remove dye and dressing. As I had not at my disposal any references on the percentage of nitrogen in the various kinds of silk, it was determined in my laboratory by the Kjeldahl process, with the following results:—

	Silk of <i>B. mori</i> .	Tussah silk.
Moisture (105°)	.. 8.85	9.10
Nitrogen (a)	.. 16.09	14.34
„ (b)	.. 16.45	14.45

But although the nitrogen of ordinary silk is thus greater in proportion than that of the tussah silk, the difference is scarcely enough to explain the difference of the odours on combustion.

Under these circumstances chemical tests must, for the present, be laid aside in the detection of tussah silk, and our reliance must be placed on microscopic examination.—*Chemiker Zeitung*.

DETERMINATION OF ANILINE IN PRESENCE OF SMALL QUANTITIES OF TOLUIDINE, AND THE DETERMINATION OF TOLUIDINE IN PRESENCE OF SMALL QUANTITIES OF ANILINE.*

By P. DOBRINER and W. STRANZ.

SOME time ago H. Reinhardt (*Chemiker Zeitung*) gave a method for the determination of aniline in its mixtures with toluidines. A basis was thus given for the examination and valuation of those very important products, the aniline oils.

The method depends on the fact that the action of nascent bromine converts aniline into a ter-bromine derivative and the toluidines into dibrom derivatives.

The bromine liquid is standardised with pure aniline, and the standard for toluidines is then found by multiplication with—

$$\frac{160.5}{93} \text{ (see below).}$$

If the aniline oil contains only a mixture of aniline and the two toluidines and is perfectly anhydrous, a direct

* A communication from the analytical laboratory of the Colour-Works formerly F. Bayer and Co.

titration gives both the proportion of aniline and that of both the toluidines.

The calculation of the proportion of aniline appears, from the equation,—

$x = 2.3777 vt - 1.3777 a$, in which a = the quantity of aniline oil used.

x = the quantity of aniline present.

t = the standard of the bromine liquor for pure aniline.

v = the number of the c.c. of bromine liquor consumed.

$a - x$ is then the quantity of the toluidines present in the aniline oil.

We have undertaken to test the applicability of this method if one of the components is present only in a small quantity.

The examination and valuation of the aniline oil for blues, of ortho- and para-toluidine, has been effected hitherto by the determination of the physical constants,—boiling-, fusion-, and congelation-points, specific gravity, solubility, &c. All these investigations admit of a conclusion as to the purity of the specimens in question only if executed with the most anxious care. An accurate determination of the impurities present is not thus rendered possible, and it was therefore of interest to ascertain if Reinhardt's method is sufficiently accurate for the purposes above mentioned.

As appears from the analyses quoted, the method admits of the detection and determination of small quantities of toluidine in aniline. The formula above given can be used in calculating the results.

On the contrary, the methods prescribed by Reinhardt for the titration of aniline alone, or in its admixtures with small quantities of aniline, give results not perfectly accurate. On applying the aniline standard we find in pure toluidine the presence of aniline, and in mixtures of toluidine with small quantities of aniline the proportion of the latter comes out too high. If we use, in titrating pure toluidine, the standard for toluidine calculated from the aniline standard, we obtain a result too high by about 1 per cent. The cause of this phenomenon is perhaps, on the one hand, that the error made in calculating the toluidine standard from that of aniline is double, and, on the other, that in the toluidines the substitution is less smooth than in the titration of aniline.

In paratoluidine the substitution ensues at first slowly, and we therefore, to avoid loss of bromine, add the bromine lye less rapidly. When the reaction is at once initiated, the titration proceeds here smoothly to completion.

In the titration of both toluidines a yellow colouration of the substitution products is observed, due probably to a slight oxidation.

It is also not impossible that in this kind of bromation there are formed small quantities of a mono-substitution product, which tell in the titration of pure toluidine or in presence of small quantities of aniline. If both constituents are present in about equal quantities in aniline oils, or if the aniline predominate, an error occasioned by the formation of a mono-substitution product would not come into consideration. We are still engaged with ascertaining the exact cause of the phenomenon above mentioned.

We have now found that Reinhardt's formula is sufficiently applicable in the examination of toluidine or its mixtures with small quantities of aniline, if we complete the standardising of the bromine lye for pure toluidine, and inversely calculate the standard for aniline by multiplication with—

$$\frac{93}{160.5}$$

In general it may be recommended to standardise both or pure aniline or pure toluidine. Let t and T be the

corresponding standards. The proportion of aniline x will then follow from the equation—

$$\frac{x}{t} + \frac{x - a}{T} = V.$$

As a matter of course Reinhardt's method permits of the examination of the salts of aniline and the toluidines. The determination must be effected also in the anhydrous substances dried over sulphurous acid. The examination of aniline hydrochlorate, the aniline salt of commerce, is especially important:

Reinhardt's formula then passes into the following:—

$$X = 2.5102 V T - 1.5102 A.$$

Here signify—

A = the quantity of aniline salt taken.

X = the proportion of aniline hydrochlorate therein contained.

T = the standard of bromine lye for pure aniline hydrochlorate, which may also be obtained from the aniline standard t on multiplication by—

$$\frac{129.5}{93}$$

V = the number of the c.c. of bromine lye consumed.
—*Zeit. Anal. Chemie.*

CHEMICAL VERSUS BACTERIOLOGICAL EXAMINATION OF POTABLE WATER.

By W. P. MASON.

APPROPOS of the recent articles upon this question, which have appeared in the English papers, it is noteworthy that there is a growing tendency among physicians and civil engineers to belittle the chemist's opinion regarding the potability of a water, and to pin their faith exclusively upon what the bacteriologist may have to say upon the subject. This feeling is strengthened by the publication of the results of such trials as that undertaken by the London Local Government Board, in which, it will be remembered, water samples purposely inoculated with typhoid germs were sent for analysis to one of England's leading chemists, and were by him pronounced pure.

Those who set special value upon such a "test" of methods as the above, and who consider it quite final as showing the inability of chemistry to detect pollution in a liquid which the bacteriologist would instantly pronounce very foul, should remember that such a sample of water could not be found in practice, and that the very conditions under which it was prepared eliminated the chemical items indicating pollution, while it increased tremendously the signs governing the bacteriological side of the case.

The bacteriologist sought for the Eberth bacillus, and, very naturally, quickly found it in a water purposely sown with a culture of the germ.

The chemist looked for those elements which always occur in sewage-laden water, whether the sewage be from sources of disease or otherwise, and, not finding them, he pronounced the water to be what it really was, free from sewage addition.

Sewage, as it occurs in practice, contains an immense deal of material other than that productive of disease, and it is upon just this comparatively harmless, but constantly present material, that the chemist relies for the indication upon which he bases his opinions.

He is unable to say whether or not a sewage-laden water is disease-bearing on any particular date, for to him all sewage is alike; but he condemns the water, for the reason that, although it may be harmless to-day, it is impossible to predict what may be its condition to-morrow.

Within the week I have been requested to make a

bacteriological examination of the water of a certain well, in order to determine if it be affected by neighbouring cesspools.

The physician who made the request was impressed with belief in the paramount value of such an examination and the comparative uselessness of chemical analysis.

I am quite convinced that, had I followed his suggestion, I should have sought in vain for any specific microbe; but inasmuch as upon chemical analysis I found that the "chlorine" ran twenty-four parts per million, which is about ten times the local "normal," and the "nitric nitrogen" read nine parts per million in place of 0.116, I condemned the water off hand without going further.

There is simply no comparison between the two methods in question for water problems of this class, and the value of chemistry is still more pronounced in those instances where it is possible to introduce common salt or lithium chloride into a source of suspected pollution, and then look for increased chlorine or presence of lithium in the water of the well. In legal cases touching upon this point of contamination of wells, by cemeteries for instance, the chemical testimony is especially strong.

In the matter of determining the suitability of a stream for city supply, the services of the bacteriologist should be unquestionably secured, but it is doubtful if his report can be considered of more importance than that of the chemist.

Chemical analysis, by comparing the water taken at the site of the proposed intake with that from the same stream above all points of possible pollution, can indicate whether or not up-stream contamination is felt at the lower point; nor is it necessary that the polluting sewage be from pathogenic sources in order that its presence may be recognised.

As Dr. Dupré has pointed out, chemistry in such cases anticipates what may happen in the future, and, by timely advice, may prevent an outbreak of disease, while, on the other hand, the discovery of disease germs in a water is only possible after the water has become infected.

Bacteriology is of especial value, and greatly superior to chemistry for the testing of filters and watching any variation in their efficiency.

For this purpose the simple count of germs per c.c. is most valuable, and differentiation is a secondary matter; for the assumption is a just one, that a filter which will remove the harmless bacteria will take out the objectionable ones as well.

It is very far from my desire to decry the value of bacteriology; but I cannot but feel that, in their enthusiasm over the great triumphs of the new science, the people at large have gone slightly "bacteria mad," and are apt to expect more than can be furnished by the means and information now available.—*Journal of the American Chemical Society*, vol. xviii., No. 2, Feb., 1896.

A REVISION OF THE ATOMIC WEIGHT OF ZINC.*

FIRST PAPER: THE ANALYSIS OF ZINCIC BROMIDE.

By THEODORE WILLIAM RICHARDS

and
ELLIOT FOLGER ROGERS.

(Continued from p. 227).

Balances and Weights.

THE preliminary determinations were made upon a long-armed Becker balance with the help of very carefully standardised platinised brass weights. The final deter-

minations were made upon the admirable Troemer balance procured for the research upon copper, and subsequently used for those upon barium and strontium. The weights used in these final determinations were the same as those used in the researches just cited; they were compared with one another at the beginning and at the close of the research, with satisfactory results. All weighings were made by substitution, the tare weights being vessels as nearly as possible similar to those being weighed; and all were reduced to the vacuum standard by the usual formula.

The Specific Gravity of Zincic Bromide.

In the course of recent investigations upon the atomic weights, so many of the usually accepted specific gravities of hygroscopic substances have been found to be seriously in error, that it seemed advisable to re-determine the constant which influences the reduction to vacuum of the present results.

Pure zincic bromide was dried for a long time at a temperature of 200°, and then fused and heated for a short time at 300°. The pycnometer, in which this drying was effected, was then stoppered and cooled in a desiccator. Carefully dried toluol, having a specific gravity of 0.8646 at 20°, when referred to water at 4°, was used as the liquid to be displaced. Toluol is convenient for the purpose, because so few inorganic substances are soluble in it, and because its volatility is not so great as to cause serious loss during the weighing, but is great enough to allow of the rapid drying of the exterior of the apparatus. The first sample of zincic bromide was made from very pure hydrobromic acid and ordinary pure zinc, and was distilled in an atmosphere of carbon dioxide; the second was made from the purest electrolytic zinc and the purest bromine. Both samples gave a perfectly clear dilute solution in water after the expulsion of the toluol on the steam-bath after the experiment. The decanted toluol left upon evaporation on the steam-bath only a trace of residue, which was insoluble in water. Water decanted from this residue gave no trace of precipitation with argentic nitrate; hence it is evident that zincic bromide is insoluble in toluol. The liquid contained in glass increases about 0.001 of its apparent volume for each degree of temperature; and the small appropriate correction is applied below.

Specific Gravity of Zincic Bromide.

No. of expt.	Weight of ZnBr ₂ . Grms.	Temperature. Degrees.	Weight of toluol displaced. Grms.	Water at 40° corresponding to toluol. Grms.	Sp. gr. of ZnBr ₂ at 20°.
1.	3.8856	19.8	0.7960	0.9206	4.220
2.	11.2394	20.3	2.303	2.664	4.218

Average.. .. 4.219

The value 4.22 is used in the work which follows. In this connection it may be of interest to compare the specific gravities of the substances recently determined here.

Specific Gravities compared with Water at 4°.

Substance.	Old values.	Former experiments.	New values.	Temperature.
Anhydrous BaCl ₂	3.85	{ Quincke Favre & Volson Schroeder }	3.86	24°
BaBr ₂	4.23	Schiff	4.79	24°
SrBr ₂	3.96	Bödeker	4.22	24°
ZnBr ₂	3.64	Bödeker	4.22	20°
Crystallised BaCl ₂ ·2H ₂ O	3.05±	{ Joule & Playfair Schiff Schroeder }	3.10	24°

Preliminary Analyses of Zincic Bromide.

Preparation of Zincic Oxide.—The zincic bromide used for the first series of experiments was made by the action of pure hydrobromic acid upon pure zincic oxide.

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*. Presented April 10, 1895.

For the preparation of the oxide, "pure" zinc of commerce was dissolved in pure dilute sulphuric acid, and the solution was allowed to remain over an excess of the metal for several weeks. The filtered solution was acidified with sulphuric acid, warmed, and treated with well-washed hydric sulphide, until a considerable mass of pure white precipitate had formed.

observed that the sodic carbonate occluded in the quantitative precipitation of zinc may be easily removed in this way, and the present experience showed that occluded zinc chloride could be washed away with equal ease. The zinc oxide thus obtained was almost white, with a very faint tinge of yellow; upon solution in nitric acid it gave absolutely no opalescence with argentic nitrate. Its

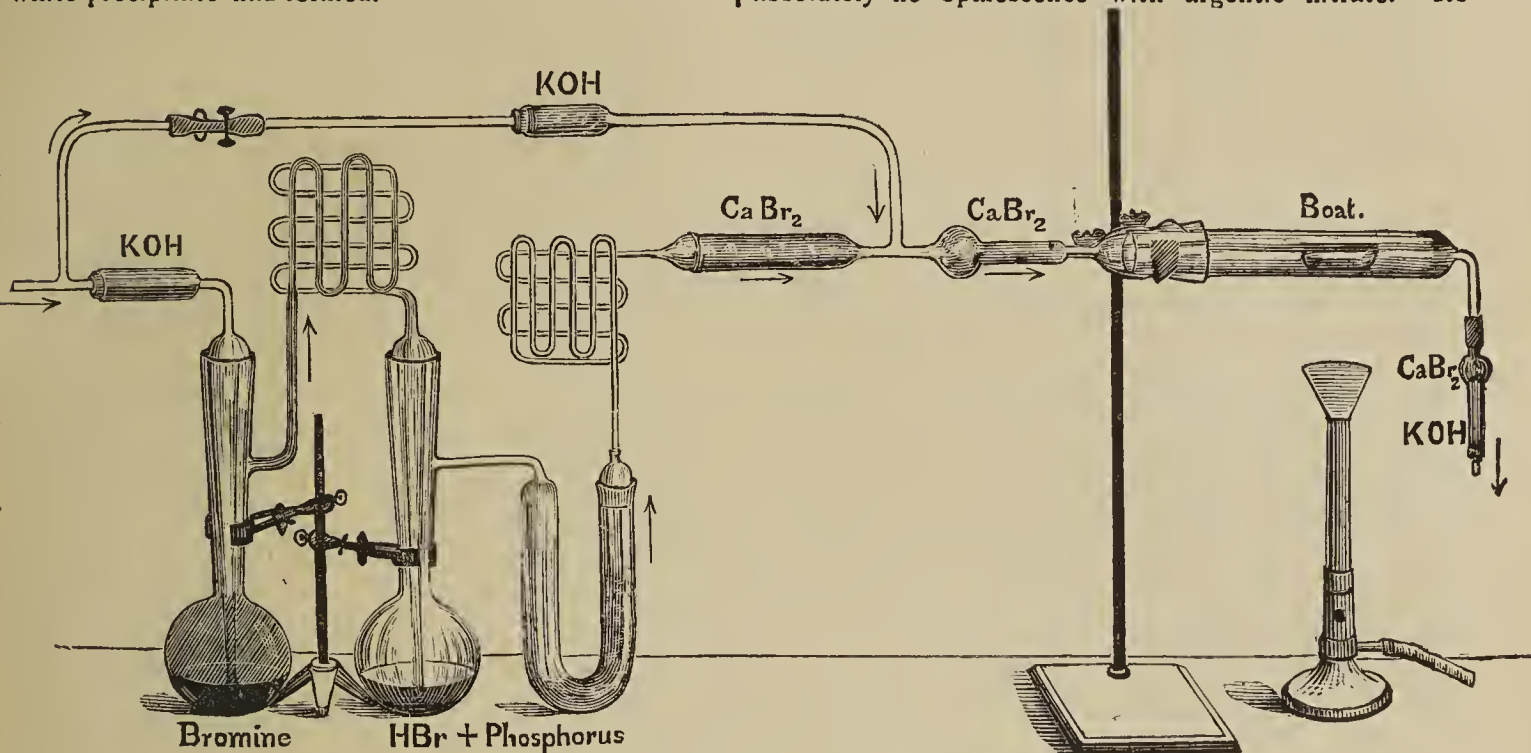


FIG. 1.—APPARATUS FOR FUSING ZINCIC BROMIDE.

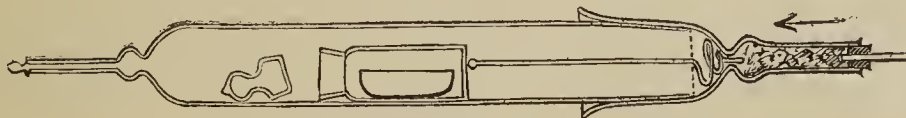


FIG. 2.

(Pure dry nitrogen and argon enter the apparatus (Fig. 1) through the tube at the left. The arrangement for preparing this mixture is not shown. Upon closing the pinchcock in the upper left-hand corner the gases are driven through the flasks and charged with dry hydrobromic acid; upon opening the pinchcock, the hydrostatic pressure causes the gases to flow through the upper short cut tube and effectually to sweep out the acid from the fusion tube. This latter tube, containing the boat in which the zincic bromide is fused, is at the right of the figure).

The strongly smelling filtrate from this zincic sulphide, now freed from all traces of the most usual metallic impurities, was treated with chlorine water to oxidise any iron or manganese which might be present, and precipitated fractionally with pure sodic carbonate. The first fraction of the precipitate containing traces of iron and manganese was thrown away.

After a thorough washing, the second fraction, containing most of the zinc, was dissolved in pure nitric acid, keeping the carbonate in excess. After filtration, the addition of a little ammonic carbonate, and another filtration, the greater part of the zinc present was precipitated by means of ammonic carbonate. When it had been subjected to a thorough washing, the basic zincic carbonate was ignited in a double platinum crucible over an alcohol lamp. The oxide thus obtained was washed repeatedly with water; for often an impurity which is held by a wet precipitate may be washed out when the precipitate has been partially decomposed or disintegrated by heat. Artus (Berzelius, *Jahresberichte*, xxiii., 132) has

method of preparation made the presence of non-volatile impurities almost impossible, for it was precipitated from a solution containing nothing but zinc, nitric acid, and ammonia.

Preparation of Hydrobromic Acid.—This substance was made by the action of bromine on water in the presence of phosphorus. The bromine was purified by the well-known method of Stas (*Mém. Acad. Belg.*, xliii., Pt. 2, 90, 38), having been dissolved in a saturated solution of potassic bromide holding zinc oxide in suspension, and distilled from this solution after long standing. The bromine, thus freed from chlorine and iodine, was collected under water and re-distilled. Red phosphorus was now purified by very fine pulverisation under water and by repeated washing of the powder with pure water. According to Stas, this method removes every trace of chlorine which may be held by the substance. Our own experience has not been uniformly favourable in this respect, but upon this occasion and several others both the qualitative tests for the absence of chlorine and the quantitative analysis of the hydrobromic acid made with the assistance of well washed phosphorus were satisfactory. The bromine was allowed to act upon the phosphorus and water with the usual precautions in an apparatus made wholly of glass. The acid thus formed was distilled in five fractions, of which the first consisted chiefly of water and a trace of bromoform. Only the last fraction of the distillate containing perhaps a third of the bromine taken, was used in the work; and this was re-distilled with the further rejection of the first and last portions. The remainder was analysed quantitatively

with pure silver in order to test its freedom from chlorine, with very satisfactory results. The silver was prepared, weighed, and dissolved with great care, the precipitate was collected upon a Gooch crucible, and all weighings were reduced to the vacuum standard.

Purity of Hydrobromic Acid.

No of experiment.	Weight of silver.	Weight of argentic bromide.	Per cent of silver in argentic bromide.
3.	1.86058	3.23884	57.446
4.	1.72320	2.99983	57.443

Average.. .. 57.444
Stas found 57.445

Preparation of Zincic Bromide.—For Experiments 5 and 6 zincic bromide was made by simply dissolving in a platinum dish the pure oxide in the pure acid described above. For Experiment 7 similar zincic bromide was sublimed in a wide glass tube in a current of pure dry carbon dioxide. The next experiment, No. 9, was made with similar zincic bromide prepared wholly in glass and not sublimed. A large portion of the substance was then prepared by exact neutralisation and evaporation in a platinum dish, a strip of pure zinc was added to precipitate a trace of platinum—which had been dissolved because of the presence of traces of oxidised nitrogen in the oxide—and the whole was subjected to crystallisation. The mother-liquor served for Analysis 8, and the pure white crystals for the third series of preliminary determinations (Experiments 10, 11, 12, and 13).

Preparation of Silver.—This substance was prepared by the method described in a recent paper on the atomic weight of barium (*Proc. Amer. Acad.*, xxviii., 22; xxix., 64).

Pure argentic chloride was reduced by means of pure sodic hydrate and invert sugar, and the metal was washed and fused in a gas flame upon charcoal. The lumps thus obtained were dissolved in pure nitric acid and precipitated by electrolysis. The beautiful crystals of electrolytic silver were rapidly fused upon cupels of sugar charcoal (*Proc. Amer. Acad.*, xxix., 65) in the flame of illuminating gas, and cooled in a reducing atmosphere. Such silver is essentially identical with the much more carefully prepared metal used in the final experiments, and gives every evidence of being pure within two or three parts in a hundred thousand (*Proc. Amer. Acad.*, xxix., 65). A solution of argentic nitrate through which over 50 grms. of such silver had passed by electrolysis, was found upon suitable treatment to yield only half a m.grm. of baric sulphate; hence the silver could not have contained more than two parts of sulphur in a million.

Preparation of other Materials.—Nitric acid was repeatedly distilled, the last portion of the distillates being used. It is needless to say that it was wholly free from halogens. The sulphuric acid used for analytical purposes was distilled with great care; that used for desiccators was boiled with a little ammoniac sulphate. The water used in the preliminary determinations was twice distilled in a tin condenser. In order to avoid the introduction of chlorine, carbon dioxide was prepared at first from acid sodic carbonate and sulphuric acid, later from dilute nitric acid and marble. Nitrogen mixed with argon was prepared by passing a mixture of air and ammonia over red-hot copper. Both gases were very thoroughly washed.

Methods of Analysis.—The necessity of driving out every trace of water from the substance to be analysed was the precaution upon which most labour was expended. The low boiling-points of zincic bromide makes it possible to distil the substance easily in a hard glass tube. Accordingly, for the first series of very crude experiments pure zincic bromide was distilled in a tube provided with bulbs, which were sealed off when filled. In order to obviate the introduction of an error from the additional weight of the atmosphere of carbon dioxide in which the

distillation took place, the bulbs were heated to about 120° at the moment of sealing. The bulbs were weighed after scratching them upon each end with a file; and after the zinc bromide had been dissolved out the glass was weighed alone. The bromine present was weighed as argentic bromide, and the atomic weight of zincic was calculated from the ratio of argentic and zincic bromides. The more trustworthy results ranged from 65.40 to 65.54, with an average of 65.47; but it was clear that the method admitted of too many possibilities of error to yield satisfactory results.

Hence the method which answered well in the recent analysis of strontic bromide (*Proc. Amer. Acad.*, xxx., 369) was adopted here. The pure re-crystallised or sublimed zincic bromide was placed in a platinum boat and kept for some time in an atmosphere of pure dry nitrogen charged with pure hydrobromic acid. It was found that in this way all the water could be expelled from the salt without the introduction of a trace of oxybromide; indeed, zincic bromide which by rapid heating in the air had been partly decomposed could be speedily brought back to its normal condition by fusion in the atmosphere of dry dilute hydric bromide. The presence of the insoluble oxybromide is easily detected by dissolving the bromide in large amounts of water; in every case the bromide used in the analyses below gave an absolutely clear solution. Baric and strontic bromides ignited in the same way give solutions which are absolutely neutral to methyl-orange and phenolphthalein; hence it is most likely that the zincic bromide, which does not admit of similar alkali-metric testing, is also quite normal. For the details the paper upon strontium must be consulted, but a sketch of the apparatus will probably suffice (Fig. 1). In the present case hydrogen could not be added to the nitrogen for fear of reducing some of the zincic bromide; but no trouble was experienced from corrosion of the boat. When the substance had been kept for some time in a state of tranquil fusion, and had just solidified, the boat was quickly slid into a weighing tube, which was in its turn placed in the automatic desiccator tube (Fig. 2). After the tube and boat had been heated to about 200° for some time in a current of pure dry air, the desiccator tube was raised to a vertical position, the stopper being thus allowed to fall into place.

After weighing, the pure zinc bromide was dissolved in water and precipitated by means of a slight excess of very carefully weighed pure silver in very dilute solution. The argentic bromide was collected upon a Gooch crucible, the shreds of asbestos carried through (0.05 to 0.20 m.grm.) were collected upon a very small fine filter, and the total weight of the argentic bromide thus obtained gave one ratio upon which to base the atomic weight of zinc. In the third series the filtrate was all evaporated to very small bulk, and the excess of silver precipitated by hydrobromic acid and weighed upon a Gooch crucible in the same way as the other portion of argentic bromide. By subtracting this excess from the total silver originally weighed out, the weight of silver equivalent to the zincic bromide could be easily found. Great care was taken to exclude daylight, and to carry out all the precautions necessary in accurate work. The data are given below:—

SECOND SERIES.

The Ratio of Zincic Bromide to Argentic Bromide.

No. of analysis.	Weight of zincic bromide. Grms.	Weight of argentic bromide. Grms.	Atomic weight of zinc.
5.	1.69616	2.82805	65.469
6.	1.98198	3.30450	65.470
7.	1.70920	2.84949	65.487
8.	2.35079	3.91941	65.470
9.	2.66078	4.43751	65.400

Average.. .. 65.459

THIRD SERIES.

The Ratio of Zinc Bromide to Silver and Argentic Bromide.

No. of anal.	Weight of zinc bromide. Grms.	Weight of silver. Grms.	Weight of argentic bromide. Grms.	Atomic weight of zinc from $\text{Ag}_2 : \text{ZnBr}_2$.	Atomic weight of zinc from $2\text{AgBr} : \text{ZnBr}_2$.
10.	2.33882	2.24063	3.90067	65.409	65.400
11.	1.97142	1.88837	3.28742	65.444	65.434
12.	2.14985	2.05971	3.58539	65.396	65.402
13.	2.00966	1.92476	3.35074	65.472	65.463

Average.. .. 65.430 65.425

The second series of results, excepting the last determination, is undoubtedly affected by the presence of water in the zincic bromide; for the methods of drying and transference had not been perfected. The third series was much more carefully made, but even here there was a possibility of the retention of a small amount of water in some of the analyses; hence this result also is probably somewhat too high.

The results of the four analyses of the third series give the following figures for the per cent of silver in the bromide:—57.443, 57.443, 57.447, and 57.443. The mean of these results is 57.444; Stas having found 57.445. It will be remembered that the hydrobromic acid from which the zincic bromide was made gave precisely similar results. This identity proves that the analytical work was without fault, and that argentic bromide does not possess the slightest tendency to occlude zincic bromide when precipitated from dilute solutions. The analysis of the hydrobromic acid proved that the material was free from chlorine and iodine.

Accordingly the rather large variations in the results must be due wholly to the original condition of the samples of zincic bromide. It remained, therefore, to make a final series of determinations upon zincic bromide from which water should have been absolutely excluded; and since one of us was unfortunately called away, this series was made by the other alone.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING APRIL 30TH, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, May 11th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 167 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from April 1st to April 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 167 samples examined all were found to be clear bright, and well filtered.

The amount of rain which has fallen during the past month is again very much below the average of the last 30 years. The actual rainfall was 0.58 inch, the 30 years' average being 1.66 inches, leaving a deficiency of 1.08 inches, most of the fall occurring between the 10th and 17th of the month. We may add that the total deficiency for the first four months of this year is 3.06 inches.

Our bacteriological examinations gave the following results:—

	Colonies per c.c.
Thames water, unfiltered	1833
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	60
Ditto ditto lowest	16
Ditto ditto .. (12 samples) mean	33
New River water, unfiltered	1501
New River water, from the Company's clear water well	17
River Lea water, unfiltered	1643
River Lea water from the East London Company's clear water well	34

By comparing the above figures with those of the last few months, it will be seen that the quality of the London waters is of great excellence, and that the filtering plant of the several Companies is maintained in a state of high efficiency.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
JAMES DEWAR.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 225).

The Spectrum of Trioxide of Thallium prepared from Lamy's Sulphate.—I repeated several times on trioxide the observations I had made on the metal reduced at the same time. When a platinum wire loop is plunged into well-washed trioxide of thallium, that had been quickly dried and fused in a platinum dish recently heated to whiteness to drive off the sodium derived from the air, and when the loop coated with trioxide is inserted into a hydrogen flame or Bunsen burner, or into incandescent hydrogen, the same phenomena are observed at similar intensities. Spectrum analysis shows the single green line, whether the observation be made with a very narrow slit, or with it wide enough to show a faint or strong continuous spectrum.

Thus, without doubt, the metal and its trioxide, prepared at the same time by electrolysis purified ammoniated sulphate, show the same spectrum as the sulphate itself, which consists of the single green line.

I converted the greater part of the metal and the trioxide produced by electrolysis into sulphate. Having found that the spectra of the sulphates thus produced were identical, I subjected an ammoniated solution of them separately to electrolysis. The metal and trioxide derived from each of them still showed identical spectra, characterised by the single green line. Finally, from the new metal and trioxide, I re-formed sulphates. Thallium and trioxide from the *third regeneration*, when introduced in succession into a hydrogen flame, a dark coal-gas flame, incandescent hydrogen, and finally into an oxy-hydrogen blowpipe at the highest possible temperature, showed, on spectrum analysis, either a dark or luminous spectrum, both marked with a *single and isolated green line*, incapable of being split up.

Such, in fact, is the spectrum of the metal in the sulphate of thallium prepared by the late M. Lamy.

The Flame Spectrum of Chloride of Thallium.—I converted the greater part of the metal and trioxide into sulphates, and these sulphates into chloride of thallium; after washing, it was dissolved twice in boiling water, and the solution precipitated by means of hydrochloric acid. When properly separated from the mother-liquor, by means of a wash-bottle, and introduced, on a platinum wire loop overlaid with iridium, into a pure hydrogen flame, a Bunsen flame, and into incandescent hydrogen, it showed, on analysis of these flames, a spectrum characterised by a single green line, on a dark or bright background, according to the width of the slit. The platinum wire loop was not attacked by chloride of thallium; the thallic spectrum disappeared when the chloride was volatilised,—a phenomenon which did not occur with the metal and trioxide, for they attacked and penetrated the platinum.

I shall refer later on to the position of the line shown by chloride of thallium, already fixed by M. Bunsen.

When left under a bell-jar to dry, it occluded sodium, but so slowly that it only showed the sodium line after four or five days exposure, when sheltered from air dust.

The Flame Spectrum of Carbonate of Thallium prepared by Mr. Crookes.—After having separated the small quantities of barium and calcium contained in the carbonate of thallium sent me by Mr. Crookes, this salt, when introduced into a hydrogen or oxyhydrogen flame, showed, on spectrum analysis, a spectrum consisting of the thallium and sodium lines. No other line was visible. In the last chapter I described the reason why I could not get rid of the latter line. Later on I shall return to the spectrum of pure carbonate of thallium.

The Flame Spectrum of Mr. Crookes's Thallium, and of the Metal obtained by purifying Commercial Thallium.—I described at some length, in the last chapter, the method I adopted for purifying the thallium sent me by Mr. Crookes. I applied the same method for preparing thallium from my commercial metal.

The final result having been the same, I can limit myself to saying that the metal obtained by electrolysing an ammoniated sulphate showed the same spectrum as the metal I prepared by electrolysing the ammoniated sulphate purified by the late M. Lamy. When varying the method of volatilising the metal, and working on *seven different samples*, the spectrum, dark or bright according to the width of the slit, always consisted of the same single green line. The flame spectrum of thallium is therefore absolutely the same as that originally described by Messrs. Crookes, Lamy, Bunsen, and Kirchhoff.

I will say the same with regard to the spectrum of the trioxide produced at the same time as the metal, by electrolysing the ammoniated sulphate. The vapour of this trioxide, obtained at a temperature near the fusing-point of iridium, only showed, on spectrum analysis, the single green line, on a dark or bright background, according to the width of the slit and the part of the vapour examined.

This conclusion was confirmed by the observations I made on the flame spectra of chloride, bromide, and iodide, obtained from the sulphate used to produce the thallium and its trioxide. In fact, the spectra of the three thallium compounds are identical with those of the metal derived from the sulphate, and of Lamy's sulphate, chloride, and metal.

My researches on bromide and iodide enable me to say that these compounds do not impart to a hydrogen flame that brilliant pure green tint seen with the metal, trioxide, sulphate, and chloride. With an equal amount of metal introduced into the flame, its tint is much paler and duller, and approaching to blue. It appears to me that at the temperature of burning hydrogen and coal-gas in air, and much more so at the temperature of hydrogen made incandescent by burning in oxygen, bromide and iodide are dissociated, that the bromine and iodine are set

free, and thus help to change the colour characteristic of a thallium flame.

Whatever may be the cause of it, the thallium spectrum remains the same as regards the singleness of the line.

On the Flame Spectrum of Thallous Hydrate, Carbonate, and Nitrate, obtained directly from Pure Metal.—I wished to carry my investigations as far as possible. For this purpose I converted into thallous hydrate, carbonate, and nitrate, part of the metal crystallised in large flakes, obtained by electrolysing pure sulphate. In the last chapter I described the means I used for this end.

I also had occasion to note the identity of the spectra of thallous hydrate, carbonate, and nitrate with that of the metal from which they were derived. I found, at the same time, that at the instant they were produced, hydrate and carbonate contained sodium, probably occluded from the air used to oxidise the metal, whilst the solution of nitrate did not show the sodium line immediately after the metal was dissolved in pure nitric acid; but, when left to itself to evaporate, crystallised nitrate showed the sodium line as plainly as crystallised carbonate, and that it was sufficient to re-dissolve them and precipitate the solution by means of absolute alcohol, in order to so far free them from sodium that they no longer showed the sodium spectrum with that of thallium.

From the above work I conclude that the flame spectrum of thallium, and such of its compounds as can be obtained sufficiently pure, consists simply of the single line to which we owe the discovery of the metal.

On the Electric Spectrum of Thallium and its Principal Compounds.—I commenced this research by examining the electric spectra of thallous sulphate and chloride, obtained from Lamy's sulphate. An induction spark was passed, from a coil with a condenser, capable of giving sparks 5 c.m. in length, between platinum balls from 2 to 3 m.m. apart, and coated with sulphate or chloride, fused or moistened. When using them fused, the spark was barely coloured green; on the other hand, it was a very intense pure green when the sulphate and chloride were moistened with a saturated solution of the same. On spectrum analysis of a thallic spark, passing either vertically or horizontally, and using a sufficiently narrow slit, the spectrum consisted of a single line on a dark background, the line being pure green and not very brilliant with fused sulphate and chloride, and pure green and very intense when these compounds were kept moistened.

Under the given conditions,—that is to say, with purified chloride and sulphate, and electrical phenomena of the above-mentioned intensity,—the sodium and air lines were entirely absent.

In order to ascertain the actual cause of the absence of the sodium and air lines, I substituted for the platinum balls coated with sulphate or chloride, clean platinum balls, also fixed from 2 to 3 m.m. apart. After passing a series of sparks, and noting the appearance of the sodium and principal air lines, *without breaking the current*, I coated the balls successively with a thin paste of pure sulphate and chloride. At the very moment the sparks became green, the spectrum, which was more or less luminous, owing to the air lines, became dark, the air lines and the sodium line disappeared, and were replaced by a single strong pure green line. The thallic rays from the spark masked the sodium and air lines. This property of masking is real, though very limited.

On coating the platinum balls with moistened thallous sulphate, on which a sufficient quantity of sodium had condensed, by exposure to air under a bell-jar, to show the sodium line persistently in a flame spectrum of thallium, the electric thallium spectrum showed the sodium line, although very faintly. Air lines did or did not appear, according to the relative intensity of the electrical phenomena.

The spark dissociated the thallous sulphate and chloride; it was found, in fact, that after its passage these compounds were very much blackened and coated with peroxide of thallium.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, May 8th, 1896.

Captain W. DE W. ABNEY, President, in the Chair.

MESSRS. FRITH and ROGERS read a paper on "*The True Resistance of the Electric Arc.*"

It was pointed out by Prof. Ayrton at the British Association meeting, at Ipswich, that if the "true resistance" of an arc is defined as the ratio of a small increase of the P.D. between the carbons to the corresponding change in the current, then it follows that this "true resistance" must be a negative quantity.

In order to measure the "true resistance" without appreciably altering the form of the carbons, &c., the authors superpose a small alternating current on the main continuous current. The arc lamp employed was adjusted by hand, and the arc length was measured by projecting an image of the arc by means of a lens. The main (continuous) current and P.D. were measured by a Weston ammeter and voltmeter, while the auxiliary alternating current was measured by means of an air transformer and an electrostatic voltmeter.

The authors find that between the limits employed, the magnitude of the alternating current did not influence the results obtained for the resistance of the arc.

The frequency, so long as it lies between the limits 250—7 complete alternations per second, and the waveform do not influence the resistance, since the same results were obtained with a Pyke and Harris alternator, a Ferranti alternator, a Gramme alternator, and a Mordey transformer.

For each make of carbon examined, four combinations were used: + cored, - cored; + cored, - solid; + solid, - cored; + solid, - solid. The general character of the curves obtained is that for the + solid, - solid combination, the "true resistance" is always negative; while for + cored, - cored, it is always positive. The other curves lying between these two extremes; those which have the + carbon solid always being more negative than those which have the + carbon cored.

In the case of the curves showing, for solid carbons, the relation between the resistance of the arc and the P.D. between the carbons, the current being constant (10 ampères), a minimum (maximum negative) value for the resistance occurs at about 55 volts. With combinations having a cored positive this minimum becomes more strongly marked, and occurs at a lower voltage. The authors find that for cored carbons the position of this minimum is closely connected with the presence or absence of the dark space in the arc. For points on the curve to the right of the minimum point, the dark space is absent; while for points to the left of the minimum, the dark space is always present.

It was found that the effect of using as the + carbon a Carré carbon in which the core had been bored out, was to obtain a curve closely resembling that obtained when both carbons were solid. On filling this hollow carbon with plaster-of-Paris or kaolin the resistance of the arc became positive.

The above experiments were made with the + carbon uppermost; other experiments made with the arc inverted showed that with solid carbons the resistance is not appreciably altered by inverting the arc. With cored carbons, however, the resistance, as well as the physical character, of the arc is altered; for, on inversion, the dark space disappears and the resistance considerably diminishes. If, however, the conditions under which the arc is burning are such that the dark space is absent, then inverting the arc does not alter the resistance.

Attempts were made to measure the "true resistance" of a direct current hissing arc, but it was found that even

with the alternator at rest there was a large deflection of the electrometer, showing that the current through a hissing arc was oscillatory.

In order to elucidate the marked difference between their results for cored carbons and those deduced from Mrs. Ayrton's curves, the authors have made a series of measurements at low frequencies. They find that there is a critical frequency above which the resistance has a positive value which is independent of the frequency, and below which it has a negative value: this critical frequency being between 7.5 and 0. In order to investigate the sign of the resistance at low frequencies, the vibrations of the needles of the ammeter and voltmeter were made use of. By an arrangement of mirrors, the needles and scales of both instruments could be observed simultaneously. In this way it could be seen whether the two needles were, at any instant, vibrating in the same or in opposite directions. If the needles vibrate in the same phase, i.e., if an increase of P.D. is accompanied by an increase of current, then the resistance must be positive; while if they are vibrating out of phase, i.e., if an increase of P.D. is accompanied by a decrease in current, then the resistance is negative.

An attempt to run the arc off a continuous current dynamo failed, since, even with the alternator at rest, the electrometer showed a large deflection, evidently due to the oscillation of the current, owing to the commutator of the dynamo bearing a finite number of segments.

Prof. A. GRAY doubted whether it was right to give the name "true resistance" of the arc to the slope of the curve connecting the potential difference (V) and the current (A). The authors' method of deducing $\frac{\delta V}{\delta A}$ was only true if the curve was a straight line; while in the case of the arc E and a may both vary with the current.

Mrs. AYRTON said that with reference to the question of the existence of a back E.M.F., the evidence tended to show that it did not exist. By using an exploring carbon no constant back E.M.F. could be found.

Prof. AYRTON said that, considering the arc as consisting of a back E.M.F. and a resistance, it was necessary to separate these two. Simply obtaining one value of the P.D. and the current was of no assistance in solving this question, but a series of values had to be taken. By taking the changes in the P.D. and current sufficiently small, the curve over the range considered was practically straight. It was curious to note that as long as observers obtained a positive value for the resistance of the arc, no fault was found with the method; but that now a negative value was found, the accuracy of this method was questioned. If a back E.M.F. does really exist, then it follows that the arc must have a negative resistance. Mr. Frith has shown why some people have got positive and some negative values for the resistance of the arc, and also that with an alternating current you may get either one or the other.

Mr. S. CARTER asked if the fact that the arc had a negative resistance did not imply a back E.M.F. in order that the arc might be stable. If so, was a negative resistance such an absurdity?

Mr. CAMPBELL said that he was very pleased to see that the authors had applied a method which he (Mr. Campbell) had suggested for measuring pulsating currents. If a pulsating current, such as could be obtained by means of a make and break, were passed through a thermopile you would get a back E.M.F., while if an alternating current were employed, you would not.

Mr. FRITH, in his reply, said that he had defined the "true resistance" as $\frac{dV}{dA}$. Mrs. Ayrton has shown that an arc will not run unless a certain resistance is placed in series with it; this resistance must be numerically equal to the negative resistance of the arc itself.

Prof. AYRTON said Mr. Frith's remarks as to the cause

of the want of stability of an arc without outside resistance were most suggestive.

The Chairman (Captain ABNEY) said he did not like the expression P.D. He suggested the employment of photography to facilitate the accurate registration of the instrument readings.

The further discussion on the paper was adjourned till the next meeting, on May 22nd.

NOTICES OF BOOKS.

Foods; their Composition and Analysis. A Manual for the use of Analytical Chemists and others. With an Introductory Essay on the History of Adulteration. By ALEXANDER WYNTER BLYTH, M.R.C.S., F.I.C., F.C.S., &c., Barrister-at-Law, Public Analyst for the County of Devon, and Medical Officer of Health and Public Analyst for St. Marylebone. With numerous Tables and Illustrations. Fourth Edition, Revised and Enlarged. London: C. Griffin and Co., Ltd., Exeter Street, Strand. 1896. 8vo., pp. 735.

A NEW edition of Mr. Wynter Blyth's standard work on Foods and their Adulteration, enriched, as is the one before us, with the recent discoveries and improvements effected in all civilised countries, will be accepted as a boon by public analysts and medical practitioners.

The history of the sophistication of food in the days of classical antiquity, in the Middle Ages, and even in later days, shows that the "good old times" had their shadow side, grim enough to all intents and purposes. We are apt to shudder on learning that at one time the bake-houses were used as a suitable place for disposing of the bodies of murdered persons. But we do not find that until recently sophistication was formally defended by persons of eminence—or at least of prominence—as being merely one form of the worship of the modern idol Competition. Some of the punishments inflicted of old for the adulteration of food certainly did not err on the side of leniency. Thus at Nuremberg, in 1444, one Jobst Fendeker was burnt for the crime of selling spurious saffron, and in the following year two men and a woman were *buried alive* for the same offence. In this country we should be very tolerant towards adulteration if it were limited to an article so utterly unimportant.

After the history of this rampant form of crime, we come to a view of the present state of the law in England relative to the adulteration of food, the text of the Acts of 1875 and 1879 being given in the Appendix. A careful perusal of these Acts leaves on the mind a very unsatisfactory impression. The punishments for the convicted offender—fines only—are often so low that the dealer may be quite willing to incur them for the sake of the additional gain. Repeated offences may be regarded as misdemeanours, and may be visited with imprisonment and hard labour. This penalty, though often justly incurred, is scarcely ever inflicted.

A great defect in the law as it stands is that, whilst it is invariably laid down that the money penalty inflicted in any case shall not exceed £ pounds, there is no proviso against its being reduced to a merely nominal amount. Instances of this kind are too common. The quibble based on the words "to the prejudice of the purchaser," which seem to have been introduced for the very purpose of stultifying the Act, seems to have been at last got rid of. Section 5, which makes guilty knowledge essential to the proof of the offence, is another capital flaw. It may be fairly assumed that every dealer should be able to judge of the articles which he keeps for sale. If a retailer proves, to the satisfaction of the Court, that any article concerning which question has arisen is in the same state as supplied to him by a merchant or manufacturer, the law ought to see to it that the latter receives a heavier sentence.

A useful feature of this work is that due attention is called to the use of the spectroscope in the recognition of colouring-matters. In a note the author quotes, from the *Berichte*, that magnesium salts alter, more or less characteristically, the spectrum of juice of elder-berries, the colouring-matters of the beet, dahlia, dragon's mouth, horse-chestnut, hyacinth, rhododendron, purple aster, and *Primula farinosa*.

The examination of the "ash" of foods receives a very thorough notice. The author recommends that in all cases the percentage should be determined; in such fluids as milk, the alkaline phosphates and the chlorides; in seeds like wheat and cocoa, total phosphoric acid; in beer-ash, common salt; in bread ash, presence or absence of alumina, magnesia, and proportion of silica to alumina; in tea-ash, the alkalinity, and iron, silica, and proportion of soluble to insoluble ash; and in coffee-ash, the presence or absence of silica.

The old method of determining carbon dioxide by estimation, in light glass vessels, by loss of weight, is declared to be quite forsaken.

For total nitrogen in foods the Kjeldahl process is said to be now in most frequent use.

The newest fraud in sugars is to colour inferior qualities with yellow aniline dyes, and pass them off as Demerara. Beet sugars may be distinguished from cane sugars by a comparison of the ash, which in the former contain nearly thirteen times more soda than the latter. Among sweet-meats, toffy is correctly said to be composed of butter and sugar melted together. "Butter Scotch" is probably the same article under a new name. It is rightly remarked that beet-treacle has so unpleasant a taste that it is not used in articles of food.

For the recognition of alum in flour the work before us recommends Cailletet's "chloroform" test; but to distinguish between alumina derived from alum from such as may have been introduced as clay, the logwood test plays an essential part. Alum in food in "reasonable quantities" (what are they?) is pronounced not injurious to health.

It is not sufficiently known that in putrid peas there may be generated a peculiar poison, probably a ptomaine.

Peas preserved by the addition of copper have been found to be dangerous.

Coffee has been, almost from its first introduction into Europe, a favourite mark for sophistication, and so it still continues. The present law may be unfortunately evaded by calling the article "French coffee," "Coffee as in France," or some other such name. The gross mendacity of these names will appear if we remember that in France the consumer buys his coffee unground, often indeed unroasted, and, if he prefers the use of chicory, he buys this latter product separately, and adds it to the coffee in whatever proportion he desires. It was a step in the wrong direction when in England grocers were permitted to sell the two articles in mixture but were not required to state the proportions. Some years back a patent was actually granted for the manufacture of a spurious coffee with three parts of dates roasted up with one-third their weight of coffee. The odour, the flavour, and the physiological action of coffee are entirely wanting. The vilest fraud, however, is the manufacture of spurious coffee berries. Hence the consumer can no longer protect himself by buying his coffee unground.

Two additions to the Sale of Food and Drugs Act are here urgently needed. Firstly, if the word coffee occurs in the name of any substance offered for sale, it shall be amenable to the law just as if it were called coffee simply. Secondly, it should be enacted that any person who designs, makes, sells, or offers for sale, or uses any machine, stamp, or die, by which any paste, pulp, or powder can be pressed into the shape of coffee-berries, nutmegs, gall-nuts, peppercorns, or any other seed, nut, fruit, or berry occurring in commerce, every such person shall pay a penalty of not less than £200, and every such machine, stamp, mould, or die shall be destroyed, and, further, that

no letters patent shall be granted for the production of any alleged substitute for any article of food.

The reader will perceive that many adulterants formerly used or suspected are no longer met with. The chemical student and the practising analyst will find Mr. Blyth a safe guide in this difficult subject.

Alcmbic Club Reprints. The Liquefaction of Gases.
Papers by MICHAEL FARADAY, F.R.S. (1823—1845).
With an Appendix consisting of Papers by THOMAS NORTHMORE, "On the Compression of Gases" (1805—1806). Edinburgh: Wm. F. Clay.

THE liquefaction of gases must certainly rank among the most momentous pieces of chemical work conducted during the present century. Scarcely had the idea of a gas been distinctly grasped when the question arose whether certain bodies, simple or compound, were essentially gaseous, or whether this condition did not depend on temperature and pressure. In early memoirs we read of "permanent gases," distinguished from vapours and from gases which could be liquefied.

It is not shown in these papers that Faraday was the first to effect the liquefaction of gases. On the contrary, he shows that, as early as 1797, Rumford had condensed carbonic acid. Guyton de Morveau had attempted the liquefaction of ammonia, but with very doubtful success. Sulphuric acid was liquefied by Monge and Clouet, and hydrogen arsenide by Stromeyer, as long ago as 1805. Chlorine seems to have been really liquefied by Northmore, but with hydrochloric acid his success was doubtful. Carbonic acid was probably liquefied by Babbage about 1813.

But the liquefaction of gases was first taken up systematically, and with a full account of the procedures employed, by Faraday, as shown in a paper read before the Royal Society, January 9th, 1845. He was successful with carbonic acid, hydriodic acid, hydrobromic acid, silicon fluoride, boron fluoride, muriatic acid, sulphurous acid, hydrogen sulphide, carbonic acid, euchlorine, nitrous oxide, cyanogen, ammonia. Seven of these substances—including ammonia, nitrous oxide, and sulphuretted hydrogen—were solidified. Hydrogen, oxygen, nitrogen, nitric oxide, carbonic oxide, and coal gas could not be liquefied by the resources at Faraday's disposal.

It is exceedingly interesting that in the same laboratory—that of the Royal Institution—where Faraday's researches were carried on, Professor Dewar has latterly liquefied oxygen, hydrogen, and nitrogen in considerable quantities, thus putting the finishing stone on Faraday's work and effacing the class of supposed "permanent gases." Faraday's experiments must always attract attention for their simplicity and beauty.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxii., No. 17, April 27, 1896.

Method of Action of the X Rays on the Photographic Plate.—R. Colson.—The author investigates if the X rays act upon the photographic plate directly or by the intermediary of a transformation. His experiments seem to him to favour the former supposition.

The Heterogeneity of the Radiations emitted by Crookes Tubes, and on their Transformation by Screens.—F. Le Roux.—The photographic impressions produced by the Crookes tubes have, in the author's opinion, two principal causes, the radiations emitted by the surface of one or other of the electrodes and those

emanating from the wall of the enclosure rendered phosphorescent.

Action of the X Rays on Electrified Bodies.—L. Benoist and D. Hurmuzescu.—Not adapted for useful abridgment.

On the Rays of Röntgen Electrified.—A. Lafay.—The study of the phenomena of the charge and the discharge of conductors of the Röntgen rays presents causes of error which it is very difficult to avoid absolutely. We see especially that the charge cannot exceed a certain limit in value, which depends on the form of the conductor, on its nature, and on its position within the protective enclosure.

Optical Superposition of Six Asymmetric Carbons in one and the same Active Molecule.—Ph. A. Guye and Ch. Goudet.—The authors hold that the study of amyl-divaleryl tartrate, affording an instance of the algebraic superposition of the optical actions of six asymmetric carbons in one and the same active molecule, completes demonstration of the principles which they laid down at the outset of their researches, the independence and the algebraical superposition of the optical effects.

New Basic Magnesium Nitrate.—Gaston Didier.—This compound has the composition $3\text{MgO}, \text{N}_2\text{O}_5, 5\text{H}_2\text{O}$. It is rapidly destroyed by cold water.

On Crystalline Iron Sesquiphosphide.—A. Granger.—This substance has the composition Fe_2P_3 . It is insoluble in nitric and hydrochloric acid and in aqua regia. At a bright red heat it loses phosphorus, and melts with difficulty.

A Study on Peridinitronaphthalene.—Ch. Gassmann.—An energetic nitration of naphthalene produces two new bodies, α and β binitronaphthalene, fusible at 170° . The two dinitronaphthalenes separated by means of acetone.

On Phenylhydrazine Tartrate and its Derivatives.—H. Causse.—The author has obtained a bitartrate, $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_{12}$, a double phenylhydrazine-potassium bitartrate, a double phenylhydrazine-barium compound, and a double phenylhydrazine and antimony compound.

Combustion-heat of the Cyanogen Derivatives.—M. Guinchant.—The author's results are given in the form of tables.

Distillation of the First Acids of the Fatty Series.—E. Sorel.—I have been induced to apply to mixtures of water with the first four acids of the fatty series the method of distillation by successive fractions sheltered from radiation, as I have described in the *Comptes Rendus*, cxvi., p. 693. I have operated this time in a glass flask with a curved neck plunged into a double enclosure. The neck of the flask, bent at an acute angle, traverses a copper lid lined with asbestos, so that any return of the condensed product to the body of the flask is impossible. The outer enclosure, raised by a ring of gas-burners to a temperature higher than the ebullition point of the liquid in question, gradually heats the internal enclosure in which is the flask containing 550 c.c. of the liquid being studied, and when a thermometer placed close to the neck and the body of the flask showed a temperature at least equal to that of ebullition I light a Bunsen burner under the flask and conduct the distillation slowly. The condensed liquid is collected by fractions of 50 c.c. We thus know the composition of the liquid in the flask at the moment of collecting each fraction. We put aside the first 50 c.c., which may in part have been distilled below the normal temperature of distillation. The results are given in tables.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. xxxiii., No. 3.

Detection of Silver and Gold in Iron.—H. N. Warren.—From the CHEMICAL NEWS.

MISCELLANEOUS.

The Sanitary Institute.—The Council have accepted an invitation from the city and county of Newcastle-upon-Tyne to hold a Sanitary Congress and Health Exhibition in that city in the autumn of this year.

The South African Horse Sickness.—According to a medical contemporary, Dr. Erdington, the Director of the Cape Town Bacteriological Institute, has detected the microbe occasioning the horse-disease of South Africa. Its identification was easy, but its culture was very difficult. The gum of the wild mimosa is laden with the *Mycelia*. As the disease is a great obstacle to the development of valuable tracts of land, Dr. Erdington recommends the destruction of the mimosa trees.

Royal Institution.—The Annual Meeting of the Members of the Royal Institution of Great Britain was held on the 1st inst., Sir James Crichton-Browne presiding. The Annual Report of the Committee of Visitors for the year 1895, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The real and funded property now amounts to above £100,000, entirely derived from the contributions and donations of the Members and of others appreciating the value of the work of the Institution. Seventy-two new Members were elected in 1895. Sixty-three lectures and nineteen evening discourses were delivered in 1895. The books and pamphlets presented in 1895 amounted to about 260 volumes, making, with 594 volumes (including periodicals bound) purchased by the Managers, a total of 854 volumes added to the library in the year. Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year. The following gentlemen were unanimously elected as officers for the ensuing year:—**President**—The Duke of Northumberland, K.G. **Treasurer**—Sir James Crichton-Browne, M.D., F.R.S. **Secretary**—Sir Frederick Bramwell, Bart., D.C.L., F.R.S. **Managers**—Sir Frederick Abel, Bart., K.C.B.; Sir Benjamin Baker, K.C.M.G.; John Wolfe Barry, Esq., C.B.; The Right Hon. Lord Halsbury; Charles Hawksley, Esq., M.Inst.C.E.; John Hopkinson, Esq., F.R.S.; Victor Horsley, Esq., F.R.S.; William Huggins, Esq., F.R.S.; The Right Hon. Lord Kelvin, F.R.S.; Alfred B. Kempe, Esq., F.R.S.; George Matthey, Esq., F.R.S.; Ludwig Mond, Esq., F.R.S.; Sir Andrew Noble, K.C.B., F.R.S.; The Right Hon. Earl Percy; Basil Woodd Smith, Esq., F.R.A.S. **Visitors**—Gerrard Ansdell, Esq., F.C.S.; Sir James Blyth, Bart.; Arthur Carpmal, Esq.; Sir William James Farrer, M.A., F.S.A.; Carl Haag, Esq., R.W.S.; Sir Francis Laking, M.D.; Hugh Leonard, Esq., M.Inst.C.E.; James Mansergh, Esq., M.Inst.C.E.; Lachlan Mackintosh Rate, Esq., M.A.; Felix Semon, M.D., F.R.C.P.; Henry Virtue Tebbs, Esq.; John Isaac Thornycroft, Esq., F.R.S., M.Inst.C.E.; Thomas Tyrer, Esq., F.C.S., F.I.C.; John Westlake, Esq., Q.C., LL.D.; James Wimshurst, Esq.

MEETINGS FOR THE WEEK.

TUESDAY, 26th.—Royal Institution, 3. "The Building and Sculpture of Western Europe," by Prof. T. G. Bonney, F.R.S.
— Medical and Chirurgical, 8.30.
— Photographic, 8.
WEDNESDAY, 27th.—British Astronomical, 5.
— Geological, 8.
THURSDAY, 28th.—Royal Institution, 3. "Lake Dwellings," by R. Munro, M.D., M.A.
— Chemical, 8. "Lothar Meyer Memorial Lecture," by Prof. P. Phillips Bedson, D.Sc.
— Institute of Electrical Engineers, 8.
FRIDAY, 29th.—Royal Institution, 9. "John Wesley—Some Aspects of the Eighteenth Century," by Augustine Birrell, Q.C., M.P.
SATURDAY, 30th.—Royal Institution, 3. "The Moral and Religious Literature of Ancient Egypt," by Dr. E. A. Wallis Budge, M.A.

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SESSION 1896-97.

The Courses of Instruction in ENGINEER-

ING and CHEMISTRY at the Institute's Colleges commence in October, and cover a period of two to three years. The MATRICULATION EXAMINATION of the CENTRAL TECHNICAL COLLEGE will be held on September 21st to 24th, and the ENTRANCE EXAMINATION of the Day Department of the TECHNICAL COLLEGE, FINSBURY, on September 22nd.

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Professors:—O. HENRICI, LL.D., F.R.S. (Mathematics), W. C. UNWIN, F.R.S., M.I.C.E. (Civil and Mechanical Engineering), W. E. AYRTON, F.R.S. (Physics and Electrical Engineering), H. E. ARMSTRONG, Ph.D., F.R.S. (Chemistry).

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THE ENTRANCE EXAMINATION will be held on September 22nd, and the new Session will commence on October 6th.

Professors:—S. P. THOMPSON, D.Sc., F.R.S. (Electrical Engineering), J. PERRY, D.Sc., F.R.S. (Mechanical Engineering), R. MELDOLA, F.R.S. (Chemistry).

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THE CHEMICAL NEWS.

VOL. LXXIII, No. 1905.

30 MAY 96

ON THE AMOUNT OF ARGON AND HELIUM CONTAINED IN THE GAS FROM THE BATH SPRINGS.*

By Lord RAYLEIGH, Sec. R.S.†

THE presence of helium in the residue after removal of nitrogen from this gas was proved in a former paper (*Roy. Soc. Proc.*, lix., p. 206, 1896), but there was some doubt as to the relative proportions of argon and helium. A fresh sample, kindly collected by Dr. Richardson, has therefore been examined. Of this 2500 c.c., submitted to electric sparks in presence of oxygen, gave a final residue of 37 c.c., after removal of all gases known until recently. The spectrum of the residue, observed at atmospheric pressure, showed argon, and the D_3 line of helium very plainly.

The easy visibility of D_3 suggested the presence of helium in some such proportion as 10 per cent, and this conjecture has been confirmed by a determination of the refractivity of the mixture. It may be remembered that while the refractivity of argon approaches closely that of air, the relative number being 0.961, the refractivity of helium (as supplied to me by Professor Ramsay) is very low, being only 0.146 on the same scale. If we assume that any sample of gas is a mixture of these two, its refractivity will determine the proportion in which the components are present.

The observations were made by an apparatus similar in character to that already described, but designed to work with smaller quantities of gas. The space to be filled is only about 12 c.c., and if the gas be at atmospheric pressure its refractivity may be fixed to about 1/1000 part. By working at pressures below atmosphere very fair results could be arrived at with quantities of gas ordinarily reckoned at only 3 or 4 c.c.

The refractivity found for the Bath residue after desiccation was 0.896 referred to air, so that the proportional amount of helium is 8 per cent. Referred to the original volume, the proportion of helium is 1.2 parts per thousand.

A GENERAL VOLUMETRIC DETERMINATION OF THE METALS PRECIPITABLE BY FIXED CAUSTIC OR CARBONATED ALKALIS.‡

By Prof. Dr. RUOSS.

THIS method presupposes that the metals precipitable by alkaline hydroxides or carbonates have been so far separated that only one of them is present in a solution.

Such a solution is in the first place rendered exactly neutral, so that no more free acid is present. This can be quite accurately effected with methyl-orange, even in neutral salts which have an acid reaction with litmus, such as, e.g., copper sulphate, zinc sulphate, iron sulphate, alum, &c., on the condition that acetic acid or oxalic acid is not present. In many cases, on the transition from free acid to perfectly combined acid, methyl-orange shows a change of colour, from rose to yellow, which takes place abruptly; but, as Thomson has previously shown,

this does not occur in all cases. Thomson then recommends to assume as the final point of the neutralisation the moment when a decided change of colour ensues.

I shall show that this assumption is not incontrovertible, and gives occasion for various errors.

According to Thomson's researches, 50 c.c. of normal lye required 49.95 c.c. of normal sulphuric acid until the pale yellow colour changed to a perceptible red; at 50 c.c. there occurred a distinct change to red, which, however, develops its full intensity only at 50.15 c.c. As sodium sulphate mixed with methyl-orange has a pale yellow colour, the true colour at 49.95 is pale yellow, not reddish. The latter colour is, in fact, not permanent, and if the liquid at 49.95 is heated and cooled the pale yellow colour becomes distinct. I regard it as absolutely necessary when the liquid is near the neutral point to heat and then to cool. To me, the titration method does not seem sufficiently accurate for the study of the changes of colour. Chemically pure salts, free from acid, which are mixed with alkali or acid give more accurate starting-points. The salts obtained by re-crystallisation mostly contain free acid; thus, e.g., pure zinc sulphate colours methyl-orange a rose. If the free sulphuric acid (which adheres most obstinately to zinc sulphate) is expelled by evaporation to complete dryness, it colours methyl-orange a pale yellow.

The conception of decided changes of colour is very indefinite, and from Section 16 of Thomson's memoir (*Zeit.* xxiv., p. 222) it appears that there exist inaccurate titrations.

Thomson there arrives at the result:—With methyl-orange the alumina present is almost entirely conjointly titrated.

By warming and cooling there would be, not 5.7, but 6 c.c.; that is, the entire alumina.

It is a rule to titrate with methyl orange only in the cold, but by comparing the colour in a hot solution with that in a cooled solution, we arrive—even in cases otherwise doubtful—at a sharp determination of the end of the titration. We divide the salts into two groups as regards their behaviour with methyl-orange:—

1. Salts which give a *yellow* colour in a neutral solution;
2. Salts which give an *orange* colour in a neutral solution.

The first group comprises the majority of all salts; in them, in the transition from acid to neutral, there occurs a change from rose at once to a pale yellow, and from rose by way of orange into yellow.

The orange colour, on heating, changes to yellow, and on cooling returns to an orange.

The second group comprises only a few salts which, in a neutral solution, have a strongly acid reaction with litmus, e.g., alum.

On the transition from acid to neutral, there appears merely a change from rose to orange. On heating, the orange colour is permanent or changes to a red.

In order to neutralise an acid solution, we add alkali until the red changes its colour, and we have then to note three phenomena:—

1. Red changes to pale yellow; the solution is then neutral.
2. Red turns to orange, and, on heating, the orange to a yellow.

Alkali is then added drop by drop to the cold solution till this likewise is yellow.

3. Red turns to orange; but this orange does not change to yellow on heating. The solution is then neutral.

Some examples may explain these differences.

We add to a solution of magnesium sulphate in a test-glass one drop of acid and methyl-orange (of a solution containing one grm. of the indicator per litre, we take 100 c.c. of liquid two to four drops); we heat and cool

* A Paper read before the Royal Society, May 21, 1896.

† I am reminded by Mr. Whittaker that helium is appropriately associated with the Bath waters, which were called by the Romans *Aquæ Solis*.

‡ *Zeitschrift für Analytische Chemie*.

by immersing the lower part of the glass in cold water; the upper (hot) part of the liquid is then yellow, and the lower (cold) part is orange to red. The same takes place also in cold solutions, such as dilute solution of copper sulphate; though here the difference of colour in the hot and cold liquid cannot be mistaken.

A solution of alum, to which has been added a drop of alkali and methyl-orange, appears orange, and on heating does not change to a yellow. With a drop of acid, we have a rose colour in the cold solution.

In many cases we can, from an acid metallic solution, obtain a neutral liquid by evaporating to dryness with sulphuric and nitric acid and dissolving the residue in water.

As a further indicator we use phenolphthalein. Its application depends on the following:—

If we mix a metallic solution with phenolphthalein and add alkalis (caustic or carbonated), the phenolphthalein does not show an alkaline reaction until all the metal has been precipitated. Ebullition is generally necessary.

The quantity of the metal present is then calculated from the quantity of alkali which has to be added to the metallic solution from the neutral point until the phenolphthalein turns red.

It would be a waste of time if we were to titrate to the exact point where the phenolphthalein turns red. We therefore add more alkali than is necessary, and remove the excess by adding acid until the solution is colourless. This method requires its justification; for on the addition of the acid it might dissolve the precipitate instead of neutralising the alkali of the supernatant liquid. The purpose of the addition of the acid is that one equivalent of acid neutralises one equivalent of alkali; if this does not take place, and if the equivalent of acid dissolves one equivalent of the precipitate, this equivalent of dissolved precipitate neutralises in turn one equivalent of alkali, and forms with it an insoluble precipitate. In one or other manner, one equivalent of alkali is always neutralised by one equivalent of acid.

As regards the addition of phenolphthalein, we take an arbitrary quantity; since this quantity is not taken into consideration, as the final reaction requires the indicator to be colourless.

Methyl-orange is decomposed in boiling nitric acid; hence, on neutralising, we add, if free nitric acid is present, alkali until precipitation takes place. This precipitate is then removed by the addition of dilute hydrochloric or sulphuric acid.

The details of the process can be inferred from the following examples:—

I.—Precipitation of the Metals as Oxides.

1.0999 grms. of copper sulphate was dissolved in water in a beaker glass, and phenolphthalein was then added.

One-fifth normal soda-lye was then added until the greenish blue colour passed, at 37 c.c. of lye, to a dark violet-blue. The liquid was then boiled; there was formed a black precipitate, and on removing the source of heat the supernatant liquid was colourless. After adding a further c.c. of lye, the supernatant liquid after ebullition was again colourless. We proceed further by c.c.'s until, after the addition of 45 c.c. of lye, the supernatant liquid was *intensely* red—a colour which did not disappear on prolonged ebullition.

Into the hot solution, after the subsidence of the precipitate, one-fifth normal sulphuric acid was then run drop by drop (the quantity being at most 1.5 c.c.). With each drop the liquid was gently agitated. Without any unusual skill it is practicable to effect this rotatory agitation so that the precipitate remains as far as possible at rest. Hence the precipitate does not need to be allowed to settle in order to judge of its colour. A white paper placed a few c.c. below the beaker renders it easy to decide on the colour.

After the addition of 0.8 c.c., sulphuric acid had dis-

appeared. Hence 44.2 c.c. of lye were necessary, and the quantity of copper sulphate was, therefore,—

$$44.2 \cdot 24.88 \text{ m.grms.} = 1.0997 \text{ grms.}$$

The precipitate was then dissolved in nitric acid, mixed with soda in a solid form until a slight precipitation ensued, boiled, and the precipitate was removed with one-fifth normal sulphuric acid.

Methyl orange was then added, and the liquid cooled. Soda-lye was then run in, with circular rotation after each drop, until the red colour turned to an orange. It was heated, and as, after cooling, the colour was yellow, it was neutral.

Now the actual titration commenced, proceeding as above; 44.2 c.c. of lye were used.

With the colours red and yellow we cannot, of course, speak of pure red and yellow, but of a mixed colour between these and the colour of the dilute copper solution.

It would, of course, have been simpler to evaporate the solution to dryness with sulphuric and nitric acid, to take up the neutral residue with water, and to titrate with phenolphthalein and soda-lye. But I sought to show that the neutralisation might also be effected in another manner.

It is not admissible to assume the neutral point on the occurrence of a minimal precipitate; such minimal precipitates disappear on heating, and often correspond not even to one drop of one-twentieth normal solution.

It was also attempted to carry out the determination of copper in a cold solution. It appeared thereby that the liquid standing above the voluminous precipitate of copper hydroxide became red long before the end of the titration, and an examination of the precipitate showed that it contained undecomposed copper sulphate. However, it is possible, with precipitates of small volume and with vigorous agitation, to effect the titration in the cold.

II.—Precipitation of the Metals as Carbonates.

We have here to take the circumstance into account that the carbonates are somewhat soluble even in pure water, and hence colour phenolphthalein reddish.

Thomson in his investigations arrived at the result that boiled barium or calcium carbonate is neutral to this indicator.

If we mix a solution of soda with an excess of barium or calcium chloride, add phenolphthalein, and boil for about five minutes, the liquid has a faint reddish colour, which in large strata is distinctly red against a white back-ground.

This circumstance is in part the cause that Thomson's proposed determination of lime and baryta yields no useful results.

An excess of soda is needed for complete precipitation, and on ebullition the red colour appeared long before complete precipitation.

We again added an excess of soda, and may take two ways for the neutralisation of the excess of alkali.

1. We use Warden's method (*American Chemical Journal*, iii., 1).
2. We filter, and in the filtrate we determine the excess of carbonate by acid.

The first-mentioned method is the simpler. After boiling, we allow the liquid to cool and deposit, stirring very gently, and adding drops of acid with a glass rod until the red colour disappears. The double quantity of acid is then deducted.

(The applications of the method will follow).

(To be continued).

Novel Mode of the Synthetic Preparation of Urea and of the Compound Symmetrical Ureas.—P. Cazeneuve.—The author regards guaiacal carbonate as a fruitful and interesting agent for the production of new symmetrical ureas.—*Comptes Rendus*, cxxii., No. 18.

CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Continued from p. 242).

I CHECKED the electric spectrum of thallium shown by the thallous sulphate and chloride prepared from purified Lamy's sulphate, by using successively *sulphate, chloride, bromide, iodide, carbonate, and nitrate*, prepared by myself, thallium sent me by Mr. Crookes, and thallium that I had bought. When using these compounds in a perfectly pure state I saw exactly the same spectrum, consisting of a single green line. It was the thallous nitrate, formed by dissolving the metal produced by electrolysis in nitric acid, only just distilled in platinum, which showed the electric spectrum, consisting of a single line, the most rapidly, the most surely, and with the greatest colour intensity. The luminosity was so great that it was necessary to make the slit very narrow, so as to shut off a partial continuous spectrum, and especially to use a vertical spark. By causing the spark to impinge on a solution newly made by the action of nitric acid on the metal, one is certain to obtain the single green thallium line, without either a continuous spectrum or air lines, or any other line. When using thallous nitrate containing a small quantity of nitrate of *silver*, the single thallium line was again seen. The characteristic silver lines were absent. As regards the electric spectrum of *metallic* thallium, I carried out the following experiments:—

After having completely coated with pure fused thallium either small platinum balls or small pointed cones of pure carbon, recently heated and held in a thick platinum wire, I arranged them *horizontally*, 2 or 3 m.m. apart, in front of the slit of the Steinheil spectrocope, and passed in succession an *induction spark, a discharge, or a current from a battery*, capable of forming after *previous contact* an arc equal in length to the distance between the two points, that is 2 or 3 m.m.

Spectrum analysis of the *spark or discharge* showed the green thallium line, together with a very faint sodium line on a dark background, *free from or accompanied by* air lines, according to the relative intensity of the spark or discharge.

In the spectrum formed by analysis of an electric arc, I saw the thallium line very brilliantly coloured, as well as a *weak* sodium line, but no trace of air or any other lines, whatever the *intensity and direction* of the current might be.

At the time these experiments were made, spectrum analysis of a strong spark enabled me to see a very brilliant sodium line in the spectrum, side by side with air lines.

Thus, *in air*, the electric spectrum of metallic thallium is the same as that of the chloride, oxide, sulphate, nitrate, &c., of this metal. As chloride, nitrate, and sulphate of thallium are dissociated in the spark, and form in this case black oxide of thallium, one may ask whether, when working in air, one really sees the spectrum of the metal, and not that of its oxide.

I made experiments on this point, working in a hard glass tube full of pure hydrogen, 10 c.m. long by 4 c.m. diam. I took care to heat, in a current of hydrogen, either thallium fused and cast into pointed cylinders, or thallium adhering to platinum balls or cones of pure carbon, so as to make the metal very bright, and surround the thallium by free hydrogen. As regards the thallium spectrum, the result was the same; I found, in fact, that with a weak spark the spectrum contained a single green line. *Neither the sodium nor any other line was seen.* The spectrum from *strong discharges* showed *three* lines; one sharp pale red line at division 36; the pure and brilliant green thallium line at 65.5; and a hazy, very pale bluish green line at 85.0 on the Steinheil spectrocope. Now the lines at 36.0 and 85.0 correspond to Fraunhofer's C

and F lines; they were due to the hydrogen in which the discharge took place. Having noted these facts, I looked for the blue line at 118.6, also belonging to hydrogen, but in vain, even when changing the analyser and the direction of the current.

When using the Hilger spectrocope, with its six prisms, spectrum analysis of a *weak or strong* electric arc, passing between carbon cones coated with thallium, only showed the single thallium line, although I had thus passed into the hydrogen a sufficient amount of thallium vapour to *rapidly* cover the upper part of the tube used as a reservoir with a very bright metallic coating, and in a very short time make the sides of the tube opaque.

In the spectrum of a thallic electric arc from a battery of thirty very large Bunsen cells, the intensity of the green line was very much weakened by the luminosity of the background, due to the production of a bright continuous spectrum. In order to see the line properly, I had to narrow the slit until it was almost closed. The luminosity of the background greatly exceeded that, although so great, noticed in the spectrum of thallium vapour raised to the fusing-point of iridium in an oxy-hydrogen blowpipe. *Hydrogen and other lines can therefore exist without the eye being able to detect their presence.* I can only compare the luminosity of the spectrum of a thallic voltaic arc to the luminosity seen when directing the collimator of a spectrocope of *low absorption power to the surface of the sun.* In fact, under these conditions, when using the Steinheil spectrocope, I was unable to see the Fraunhofer lines, however narrow the slit might be.

When testing, under these conditions, the possibility of observation BY THE EYE, I ought to mention that the electric spectrum of thallium consists of *a single line not capable of being split up*, exactly like the flame spectrum of this metal, and that *electricity is no more capable of dissociating it than heat.*

Since observers have found a complex electric spectrum of thallium when using thallium they have not prepared themselves, I think I am correct in concluding that the metal they used was other than that used by Bunsen, Lecoq de Boisbaudran, and myself.

There remains the description of the experiments I made to ascertain whether the position of the thallium line was the same in the flame and electric spectra.

On the Position of the Thallium Line in the Flame and Electric Spectra.

In his "Spectral-analytische Untersuchungen," M. Bunsen, whose work I have taken as a basis of comparison, because, amongst other reasons, I have a spectrocope exactly like his, assigned to the thallium line in the flame and electric spectra a difference in position amounting to 0.6 micrometer division on the luminous projection of his instrument. In fact, between the position of the centre of the sodium line in flame and electric spectra, the tables show a difference of 0.5 division. This difference is at least double the mean error admissible in measuring the position of a line in the electric spectrum, when using a micrometer with a luminous projection. I tried to find out whether this difference was due to an error in observation, or whether, in spite of the singleness of the line, the positions of the thallium line in the flame, spark, and electric arc spectra were not the same. To solve this question, I started the experiments I am about to describe.

As regards the flame spectrum of thallium, the mobility of which is great, I was soon convinced that by introducing thallium, or one of its compounds, into a hydrogen or Bunsen flame placed in front of the collimator, an error might be made amounting to 0.75 division on the luminous projection, according to the position of the flame in front of the collimator and the part of the flame into which the thallium was introduced. This may be observed whether the centre of the line is found by bringing the *cross wires alternately from right to left and*

from left to right of this centre, according to M. Lecoq de Boisbaudran's advice, or whether it is *estimated*, as those do who, when *weighing*, instead of balancing exactly by the *addition of weights*, judge of the oscillations about zero by the position of the pointer of the balance when it stops momentarily.

According to my lengthy experience, this system admits of readings being taken exact to *one-tenth*, and with practice to one-twentieth, of a scale division, though this division may be only about 1 m.m. I constantly use this method of reading, not only because of its rapidity, but especially because it dispenses with touching the lens of the spectroscope, any movement of which involves a risk of displacing the micrometer.

To obtain the greatest possible steadiness in the position of the thallium line, I was obliged to substitute for the flame of a lamp a blowpipe flame obtained by burning a mixture in proper proportions of coal-gas and air, *separately* stored under water in large quantities, under a *constant pressure* of from 2 to 3 c.m. of water, by means of the blowpipe used by Mr. Matthey for welding platinum.

On fitting a platinum nozzle with a hole about $\frac{1}{2}$ m.m. in diam., to the blowpipe, fitted with taps to regulate the supply of gas, it was possible to obtain at will a *vertical motionless* blowpipe flame (thanks to the use of screens), from 7 to 10 c.m. high and from 5 to 6 m.m. diam., coloured deep or pale blue, according to the volume of air mixed with the coal-gas in the blowpipe, and to the pressure under which the gases issued. I arranged the blowpipe on a stand with a rack, and put it on the left-hand board on the table carrying the spectroscope. I described this board in the Introduction to my "Spectroscopic Researches."*

The blowpipe was adjusted in front of the collimator so as to make the *right edge* of the flame coincide exactly with the axis of the collimator. I effected this adjustment by finding the position in which I could see a continuous spectrum appear on the background, on introducing a fine platinum wire into the blowpipe. Having adjusted the fiftieth division of the micrometer of the Steinheil spectroscope on Fraunhofer's D line, I put a point of the right edge in contact successively with thallium and the chloride, sulphate, and nitrate of this metal, on a fine platinum wire loop. I effected this contact by placing the carrier on the right-hand board, also described in the Introduction, by moving it slowly by means of its endless screw. The pitch of the screw being very fine, it is certain to penetrate into the flame only a fraction of a m.m. This slight penetration is necessary, on account of the extreme volatility of the metal and its compounds, in order to obtain a thin sheet of thallium vapour.

To eliminate any error due to the position of the blowpipe, I took the precaution of *displacing* and *replacing* the blowpipe and the carrier *after each measurement of position*, leaving the cross hairs in position. I could measure by *estimation* to from 0.05 to 0.10, the difference between the centre of the thallium line after the successive displacements and replacements. These movements could be made easily and quickly, thanks to the supports which moved by means of endless screws.

(To be continued).

Colorimetric Determination of Iron.—G. Lunge.—The author, for detecting traces of iron, especially in aluminium sulphates, makes use of the sulpho-cyanogen reaction. He transfers the iron sulpho-cyanide from the aqueous solution to one in ether, by shaking out the former with ether. It is found preferable to effect the peroxidation of the iron solution by potassium chlorate and hydrochloric acid instead of nitric acid.—*Zeit. für Angewandte Chemie*.

* See CHEMICAL NEWS, vol. lxxii., p. 204.

A REVISION OF THE ATOMIC WEIGHT OF ZINC.*

FIRST PAPER: THE ANALYSIS OF ZINCIC BROMIDE.

By THEODORE WILLIAM RICHARDS
and
ELLIOT FOLGER ROGERS.

(Continued from p. 241).

FINAL SERIES OF DETERMINATIONS.

By THEODORE WILLIAM RICHARDS.

ONE determination of the final series, No. 17, was made with the old zincic bromide in the new apparatus. The others were all made from new material prepared from electrolytic zinc and pure bromine, instead of from zincic oxide and hydrobromic acid. The electrolytic zinc was prepared with great care in the following manner:—An excess of "pure" zinc was treated with somewhat dilute pure sulphuric acid at 80° until, upon dilution, a marked amount of basic salt was formed. About 300 grms. of zinc had been dissolved; and this diluted solution was allowed to stand for many hours in contact with the zinc and the basic salt. After filtering, clean pieces of zinc were added to the solution; and no further metallic precipitate formed upon the zinc. The solution was then decanted and treated with a small amount of sulphuric acid and much hydric sulphide. After some time, the pure white precipitate was separated by decantation and filtration, and the solution was oxidised by an excess of pure chlorine. To this solution was then added enough very pure sodic carbonate to form a slight precipitate, and the mixture was allowed to stand several days with occasional stirring. The pure white precipitate, which must have contained any trace of iron remaining, was filtered off, and the sulphate of zinc was crystallised three times successively from hot water.

The solution of the last crystals was allowed to stand for two days over several grms. of the purest crystalline electrolytic zinc in a large platinum dish. At the end of that time the solution contained some basic salt, but the dish showed no sign of a metallic coating. The solution was filtered, treated with an excess of freshly distilled ammonia, and electrolysed. A thin rod of very pure zinc served as the negative pole, and a platinum wire as the positive. Six decomposing cells were run simultaneously on a shunt from a 50-volt dynamo which was being used for charging a storage battery. The current in each decomposing cell varied from 1 to 1½ ampères—if a much stronger current were used the cells became too warm. As Ramsay and Reynolds (*loc. cit.*) have suggested, it is advisable to remove the remarkably beautiful crystals from time to time as they grow; for this purpose a bent five-pronged glass fork, made from a heavy rod, was found very useful. The crystals were washed with ammonia until the washings were absolutely free from sulphuric acid, then with pure very dilute hydrobromic acid, and finally with much pure water. About 40 grms. of pure zinc thus formed were treated with an excess of pure bromine, which had been shaken with an alkaline bromide in aqueous solution, dissolved in concentrated calcic bromide, precipitated by water, and distilled under dilute pure hydrobromic acid. The Jena glass flask in which the combination took place was cooled during the reaction. The red solution was filtered in a glass funnel through asbestos, and the excess of bromine, together with any trace of iodine which may have been present, was driven off by leaving the Jena flask upon the steam-bath for some time in a very much inclined position. The diluted colourless solution was evaporated to small bulk, and the greater part of it was subjected to fractional crystallisation by cooling to zero. A portion which had crystallised twice successively from water was labelled (A);

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*. Presented April 10, 1895.

and another portion, the extreme mother-liquor remaining from two crystallisations, was labelled (C). Sample (B), the intermediate fraction, was not used in these experiments, as (A) and (C) were proved to be identical.

Before analysis, both (A) and (C) were subjected either to distillation or to sublimation. The sublimation was carried on in the lower part of a platinum retort, to which had been fitted closely a glass adapter for conducting the current of pure dry carbon dioxide. The substance to be sublimed was contained in a small platinum crucible fitted with a wire handle, by which it could be easily raised, lowered, or removed. The adapter was so arranged that the current of gas came as closely as possible in contact with the crucible, and so that any zinc bromide which might condense in a liquid form upon the glass, and thus run the risk of taking alkali from it, must return to the

From the substance used in the preliminary determinations (Expt. 17)	65.410
From new substance, not crystallised from water, but distilled in carbon dioxide (Expt. 14) . . .	65.403
From extreme mother-liquors from crystallisation (C) sublimed in carbon dioxide (Expt. 18) ..	65.404
From purest crystals (A), twice crystallised from water and sublimed (Expts. 15, 19)	65.404
From purest crystals (A), twice crystallised from water and twice distilled in carbon dioxide (Expt. 16)	65.398

Average.. .. . Zn=65.404

the metal may be obtained in the purest possible state; for if it is distilled according to Stas there is always

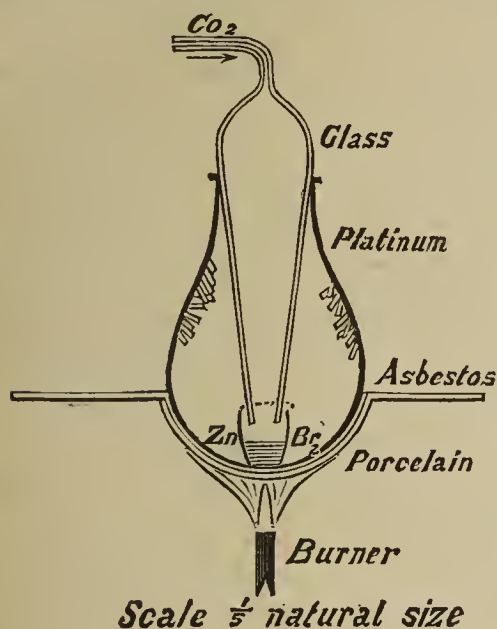


FIG. 3.

crucible and be re-distilled. The sectional drawing will give a clearer idea of the arrangement (Fig. 3).

Two powerful Bunsen burners supplied heat from below, impinging upon a porcelain dish which fitted closely to the bottom of the retort and protected the platinum. The gases from the flame were diverted by a large diaphragm of asbestos board. By means of this arrangement it is possible to sublime about half a grm. of zincic bromide an hour; the crystals are exceedingly beautiful, and give every evidence of great purity.

Instead of being sublimed, some of the pure salt was distilled in a current of carbon dioxide. For this purpose a medium sized tube of the hardest glass was drawn out so as to serve for a small retort, and this was encased in a larger hard glass tube, from which it was separated by several pieces of platinum foil. A platinum boat, into which was directed the drawn-out and turned-over point of the inner tube, served as the receiver. Here, again, a diagram must assist the explanation (Fig. 4).

The zinc bromide thus distilled possessed a peculiarly brilliant white lustre; in no case did the boat lose or gain the twentieth of a m.grm. in weight during the distillation.

The attempt was made also to distil the bromide in a vacuum, but the reduction of the pressure lowered the boiling-point too nearly to the proximity of the melting-point for convenient manipulation.

In this connection it may be well to state the atomic weight of zinc obtained from these specimens, in order to show their identity. The details of these figures are given later.

Silver.—The silver used in the final determinations was repeatedly purified by the methods already described. Finally, the beautiful electrolytic crystals were fused in a small crucible of pure lime in a vacuum. In this way

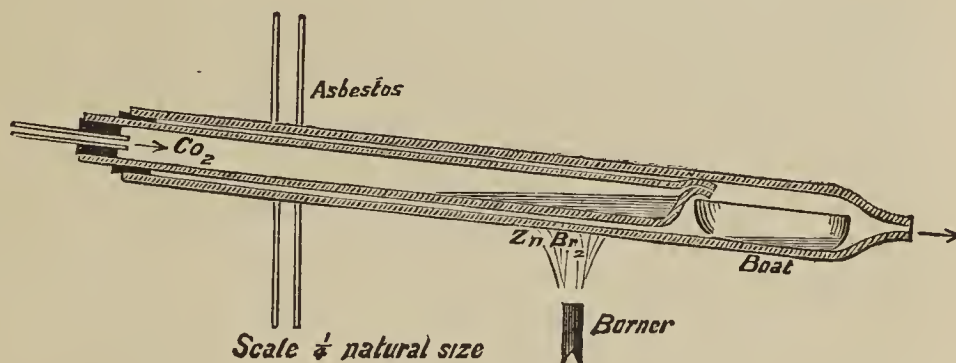


FIG. 4

danger of impurity from the oxygen and illuminating gas or hydrogen used in the oxygen blowpipe.

Other Materials.—The acids were purified in the usual fashion and the greater part of the water used was only distilled twice, rejecting the first portions. For Experiment 16, all the water used was distilled three times, once over potassic permanganate. Of course, the platinum condenser which has been already described served for all of these distillations (*Proc. Amer. Acad.*, xxx., 380).

Phosphoric pentoxide was sublimed in a stream of pure oxygen. Since the presence of oxides of nitrogen in carbon dioxide might assist the partial decomposition of zincic bromide, nitric acid was rejected as a means of decomposing marble, and very dilute hydrochloric acid was used instead. The gas was purified by passing through a solution of sodic hydric carbonate, long tubes containing argentic nitrate, and much pure water. Since the last tube containing water gave absolutely no test for chlorine after over 100 litres of the gas had passed through it, one may safely assume that the purification was sufficient. The gas was dried by means of sulphuric acid and phosphoric pentoxide.

(To be continued).

Detection of Nitric Acid in proof of the addition of Water to Wines.—F. Leon.—The processes of fermentation eliminate all traces of nitric acid existing in wines; but if traces still appear the suspicion is justified that, after the wine has been matured, an addition of water has taken place containing an impurity of nitric acid. For the detection, the author distils off the alcohol and re-distils the residue with zinc turnings, so slowly that only about 10 c.c. are obtained in half-an-hour. In this portion nitrous acid is tested for by the process of Griess.—*Gazzetta Chimica and Berichte*.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 7th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Llewellyn John Davies, 8, Wordsworth Avenue, Cardiff; Frederick William Harris, 62, Rectory Road, Burnley; John Burnett Knight, Bushwood, Wanstead, Essex; Percy Sykes Marshall, Church School House, Lockwood, Huddersfield; Loxley Meggitt, The Laurels, St. John's Street, Mansfield; Sigmund Georgjewitsch Rosenblum, 19, Russell Road, Kensington; Douglas Stuart Spens Stewart, 9, Thistle Grove, Fulham Road, S.W.; James Whitehead, Roach Place, Rochdale.

The following were duly elected Fellows of the Society:—Henry Thomas Durant, Ernest Hunter Fisher, W. Goodwin, Edgar Hawkins, John Percival Jenkins, Robert Hazlewood Jones, Herbert Edwin Macadam, John McCrae, jun., William Henry Merrett, Joseph W. Patterson, H. von Pechmann, Thomas William Pilley, Robert Barnabas Pollitt, James Proude, Charles H. Reissmann, Henry Fishwick Robinson, Otto Rosenheim, Raymond St. George Ross, Walter Dalrymple Severn, John Christopher Stead, James Edward Shum Tuckett, Edward Channing Wills, John Henry Wolfenden.

Of the following papers those marked * were read:—

*60. "Carbon Dioxide, its Volumetric Determination."

By W. H. SYMONS and F. R. STEPHENS.

After reviewing the various methods for estimating carbon dioxide in air, the authors describe one which they find to be reliable and at the same time convenient.

For collecting the samples of air they use flasks from which all air has been expelled by means of steam, their vacuity being ascertained by weighing before and after use. For absorbing the carbon dioxide, mixed solutions of sodium hydroxide and barium chloride are used. The pressure of the sample of air in the flask is made equal to the atmospheric pressure by admitting a measured volume of air free from carbon dioxide, and the true volume is found by calculation; thus the pressure, and temperature at the time of taking the sample need not be noted. The residual hydroxide is titrated, without being removed from the flask, with dilute acetic acid and phenolphthalein.

The use of the same flask for collecting and cultivating micro-organisms, estimating albumenoid ammonia and oxygen absorbing matter, is suggested, and it is pointed out that the carbon dioxide may be estimated in the same sample of air, provided the number of organisms is not sufficient to influence the results through the carbon dioxide they produce.

Examples of the trustworthy nature of the process are given; in some cases carefully measured volumes of carbon dioxide have been estimated; in others, a series of samples have been taken from a closed space occupied by the authors. A compound pipette for accurately measuring volumes of gas or liquids is also described.

*61. "On certain Views concerning the Condition of the Dissolved Substance in Solutions of Sodium Sulphate." By R. F. D'ARCY, M.A.

The differences in the solubilities of anhydrous sodium sulphate and its two well-defined hydrates, and the existence of a maximum solubility of the decahydrate at a temperature just below that at which it breaks up in the solid state into anhydrous salt and water, are properties which have been thought to indicate that these substances dissolve as such.

Other facts have been shown to be in accordance with the view that the condition of the dissolved salt is the same in all cases—the differences in solubilities being

explained as being determined by the condition of the undissolved solid in contact with the liquid.

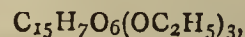
The experiments described were undertaken with the object of finding if any evidence in favour of the former, and now rather discredited, theory could be obtained by making careful experiments on the viscosities of strong solutions of this salt, prepared in different ways and at different temperatures. The results obtained are in accordance with the view of the identity of the condition of the dissolved substance in all cases.

The experimental method, which differs in some respects from those used in other researches, is believed to give results which are free from ambiguity.

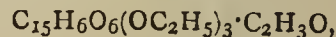
*62. "Luteolin. II." By A. G. PERKIN.

In a previous communication (*Trans.*, 1896, lxi., 206), it was shown that the formula of luteolin is $C_{15}H_{10}O_6$, a fact determined by means of its compounds with mineral acids and with bromine. The production of its tetracetyl and benzoyl compounds proved it to contain four hydroxyl groups, and on methylation it yielded a product containing three methoxy-groups. Since the publication of this paper, Herzig (*Ber.*, xxix, 6, 1013) has stated that he is also working upon luteolin. He mentions the methyl ether of the acetyl compound, and the decomposition of luteolin with fused alkalis. It is now shown that the product previously described, m. p. 210° , which, together with protocatechuic acid is formed by the action of fused alkalis upon luteolin, which did not then appear to be phloroglucol, is really this substance, as surmised by Herzig (*loc. cit.*).

On ethylation, luteolin yields a triethyl ether—



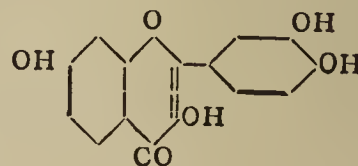
(yellow needles, m. p. $131-132^\circ$), insoluble in alkalis, which gives a monacetyl derivative—



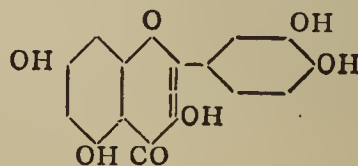
(colourless needles, m. p. $185-186^\circ$). Decomposed by alcoholic potash this ether yields a crystalline yellow potassium salt, which is resolved by water into the free ether. These reactions prove that the hydroxyl group in luteolin which resists ethylation is in the ortho-position to a carbonyl group.

When heated with alcoholic potash to $130-140^\circ$, luteolin triethyl ether yields the diethylether of protocatechuic acid, and a small quantity of a substance which gives the phloroglucol reaction. The product of the methylation of luteolin (*loc. cit.*) closely resembles the ethyl ether in its reaction, as it contains three methoxy-groups, yields an acetyl compound, m. p. $174-175^\circ$, and a yellow potassium salt. Herzig (*loc. cit.*) gives the melting-point of acetyl-luteolin $225-227^\circ$, but an examination of the melting-point previously obtained, $213-215^\circ$, shows that this must be considered as correct.

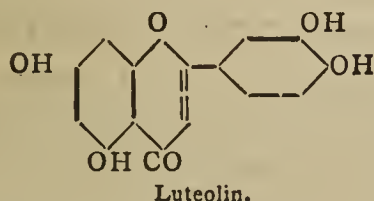
A close resemblance of luteolin to quercetin and fisetin is traced, and it is considered that quercetin, which is an hydroxyfisetin, is most probably also an hydroxyluteolin.



Fisetin.



Quercetin



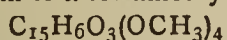
*63. "Morin." Part I. By HERMANN BABLICH, Ph.D., and ARTHUR GEORGE PERKIN.

The yellow colouring matter, morin, exists, as has been known for some time, in old fustic (*Morus tinctoria*), and has lately been shown by one of us and F. Cope (*Trans.*, 1895, 937) to be also contained in the Indian dye-stuff, Jackwood (*Artocarpus integrifolia*). By means of its compounds with mineral acids the true formula of morin was established by one of us and L. Pate (*Trans.*, 1895, lxvii., 644) to be $C_{15}H_{10}O_7$.

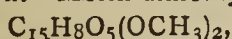
The principal reactions of morin described by previous workers are its behaviour towards alkaline reducing agents (Hlasiwetz and Pfaundler, *Fahres.*, 1864, 537), by which means it yields phloroglucol and β -resorcylic acid, and towards fused alkali, when it gives phloroglucol and resorcinol. Of the substitution products of morin but three are described, viz., morinsulphonic acid, $C_{15}H_9O_7HSO_3$ (Benedikt and Hazura, *Monatsh.*, v., 167), tetrabromomorin, $C_{15}H_6Br_4O_7$, and tetrabromomorinethyl ether, $C_{15}H_5Br_4O_7 \cdot C_2H_5$. The latter is formed by brominating morin in alcoholic solution, and can be converted into tetrabromomorin by means of zinc chloride and fuming hydrochloric acid.

The action of fused alkalis and of bromine upon morin has been investigated, and it is shown that by the former means at $150-160^\circ$ phloroglucol and β -resorcylic acid are the principal products, and with the latter the results of Benedikt and Hazura have been confirmed. Incidentally it has been found that, by the action of bromine on morin in presence of acetic acid, a considerably increased yield of tetrabromomorin is obtained.

On acetylation, tetrabromomorin yields pentacetyl-tetrabromomorin, $C_{15}HBr_4O_7(C_2H_3O)_5$ (colourless needles, m. p. $192-193^\circ$), from which it is evident that morin contains five hydroxyl groups. The principal product of the methylation of morin is a tetramethyl ether—



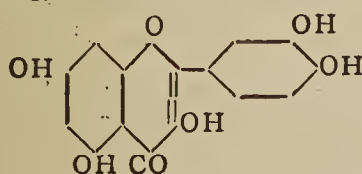
(light yellow needles, m. p. $131-132^\circ$). This substance is insoluble in alkalis, but yields a monacetyl derivative, $C_{15}H_5O_3(OCH_3)_4 \cdot C_2H_3O$ (colourless needles, m. p. 167°), and a crystalline yellow potassium salt, which is decomposed by water, regenerating the ether. When digested with alcoholic potash at $150-160^\circ$, the tetramethyl ether yields the dimethyl ether of β -resorcylic acid (m. p. $107-108^\circ$) and a small quantity of a product which gave the phloroglucol reaction. Morin dimethyl ether—



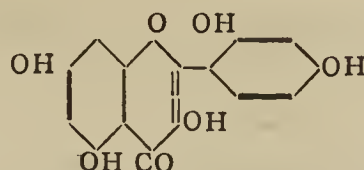
forms yellow needles melting at $255-227^\circ$.

These results demonstrate a close similarity between quercetin and morin, for both contain five hydroxyl groups, one in the ortho-position to a carbonyl group, and both combine with mineral acids. Quercetin yields with fused alkali phloroglucol and protocathechuic acid, morin, phloroglucol, and β -resorcylic acid.

The formula of quercetin appears to be (Herzig, *Ber.*, 1895, xxviii., 223)—



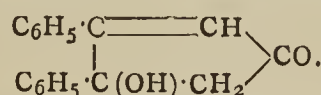
and it seems most probable that the formula of morin is represented by that of quercetin, in which the catechol nucleus has been displaced by a resorcinol group thus—



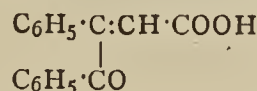
64. "Synthesis of Pentacarbon Rings. Part I. Anhydracetonebenzil and its Homologues." By FRANCIS R. JAPP, F.R.S., and G. DRUCE LANDER, B.Sc.

Anhydracetonebenzil, which is obtained by the condensation of benzil with acetone, was first prepared and investigated by Japp and Miller (*Trans.*, 1885, xlvii., 27), and was afterwards further studied by Japp and Burton (*Trans.*, 1887, li., 420). In both of these earlier communications the opinion was expressed that in the condensation a closed chain of carbon atoms was formed.

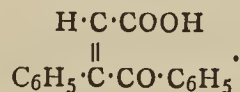
The authors now show that the compound is a diphenylhydroxycyclopentenone of the formula—



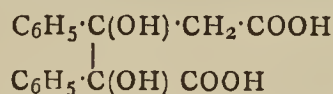
By oxidation with sodium hypobromite it gives an almost quantitative yield of Japp and Davidson's *desylene-acetic acid*—



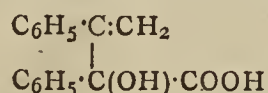
a reaction which constitutes the best means at present known of preparing this compound, and at the same time proves the configuration of the acid to be—



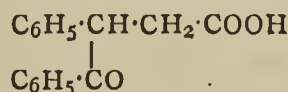
The oxidation of anhydracetonebenzil by heating it with chromium trioxide in acetic acid solution was studied by Japp and Miller (*loc. cit.*). They thus obtained a product to which they assigned the constitution of a β -benzoylhydrocinnamic (desylacetic) acid. Desylacetic acid has, however, been since prepared by Victor Meyer and Oelkers. The present authors find that the two substances are quite distinct. They also find that Japp and Miller's acid is not the primary product of oxidation, for, when the process is conducted in the cold, simultaneous oxidation and hydration occur, and *diphenyldihydroxyglutaric acid*—



(m. p. 120° , when rapidly heated), is formed. On heating this acid for some time at 100° it decomposes, parting with carbon dioxide and water, and yielding Japp and Miller's acid, which has the formula of an *isocinnamemylmandelic acid*—



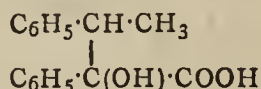
and which melts at $159-160^\circ$. (The melting-point, 152° , given by Japp and Miller is too low). When boiled with fuming hydriodic acid, or with fuming hydrochloric acid, diphenyldihydroxyglutaric acid also parts with carbon dioxide and water; but the carbon dioxide is in this case furnished by the other carboxyl group, and *desylacetic acid*—



(m. p. 162°), is formed. Beyond the close approximation of the melting-points, there is hardly any resemblance, either physical or chemical, between these two isomerides, desylacetic acid and isocinnamemylmandelic acid.

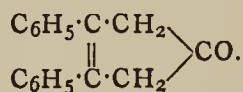
By a partial reduction of isocinnamemylmandelic acid

by boiling it for a few minutes with hydriodic acid, it is converted into *isophenethylmandelic acid*—

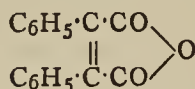


(m. p. 134—136°).

By partial reduction of anhydracetonebenzil with hydriodic acid, Japp and Burton obtained a compound, $\text{C}_{17}\text{H}_{14}\text{O}$, melting at 110°, which yielded a hydrazone, and therefore contained the original carbonyl group of the anhydracetonebenzil. The authors show that this reduction compound has the formula of a *diphenylcyclopentenone*,—

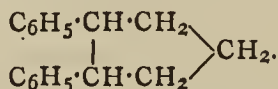


That the foregoing change in the position of the double bonds has taken place during the reduction is shown by the fact that the compound yields, on oxidation with sodium hypobromite, diphenylmaleic acid, which, when liberated from its salts, changes into the very characteristic anhydride,—

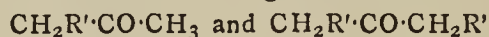


(m. p. 156°).

The hydrocarbon, $\text{C}_{17}\text{H}_{18}$ (m. p. 47°), obtained by Japp and Burton by the complete reduction of anhydracetonebenzil with hydriodic acid and amorphous phosphorus is a *diphenylcyclopentane*,—



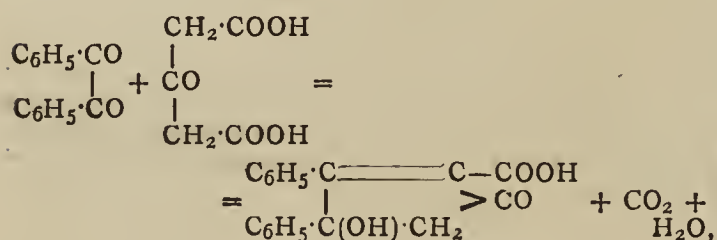
The various compounds obtained by Japp and Burton (*Trans.*, 1887, li., 431) by the condensation of benzil with homologues of acetone of the general formulæ—



must be regarded as homologues of anhydracetonebenzil.

65. "Synthesis of Pentacarbon Rings. Part II. Condensation of Benzil with Acetonedicarboxylic Acid." By FRANCIS R. JAPP, F.R.S., and G. DRUCE LANDER, B.Sc.

Benzil and acetonedicarboxylic acid, when gently warmed with dilute alcoholic potash, condense according to the equation—



yielding *anhydracetonebenzilcarboxylic acid* (m. p. 167—168°), which corresponds with *isophenanthroxyleneacetic acid* (Japp and Klingemann, *Trans.*, 1891, lix., 2).

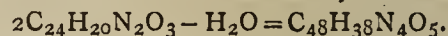
When anhydracetonebenzilcarboxylic acid is boiled for a few minutes with fuming hydriodic acid, it is reduced, simultaneously parting with carbon dioxide and yielding a *diphenylcyclopentenone* (m. p. 110°), identical with that obtained from anhydracetonebenzil itself (see preceding note).

By oxidation with sodium hypobromite, anhydracetonebenzilcarboxylic acid yields a mixture of *diphenylmaleic* and *diphenylfumaric acids*, these two substances being produced in approximately equal quantity. A change in the position of the double bonds takes place during this process.

When oxidised with chromium trioxide in acetic acid solution it parts with 2 atoms of hydrogen, yielding an

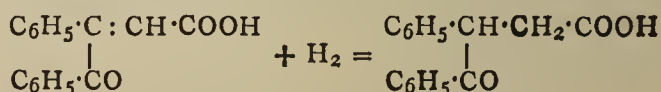
acid of the formula $\text{C}_{18}\text{H}_{22}\text{O}_4$ (m. p. 201°, with decomposition).

The action of phenylhydrazine is complex. The primary product is a yellow compound, apparently the hydrazone; but this readily changes, especially on recrystallisation, into dark red needles of a substance melting indefinitely above 200°, formed by elimination of 1 mol. of water from 2 mols. of the hydrazone,—

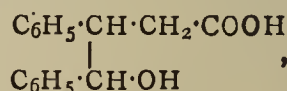


66. "Reduction of Desyleneacetic Acid, and the Constitution of Zinin's Pyroamaric Acid." By FRANCIS R. JAPP, F.R.S., and G. DRUCE LANDER, B.Sc.

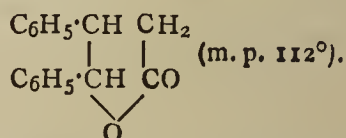
The authors find that by the action of zinc dust and acetic acid on desyleneacetic acid the latter is converted into Victor Meyer and Oelkers's *desylacetic acid*,—



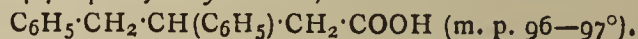
By the limited action of sodium amalgam on an aqueous solution of sodium desyleneacetate the same product is obtained. Excess of sodium amalgam, however, carries the reduction further, and $\beta\gamma$ -*diphenyl- γ -hydroxybutyric acid*,—



is formed, which, when liberated from its salts, speedily changes into the lactone—



By boiling desyleneacetic acid for four hours with hydriodic acid and amorphous phosphorus, it is converted into $\beta\gamma$ -*diphenylbutyric acid*,—



Comparison of this substance with a specimen of *pyroamaric acid* showed that the two were identical. Pyroamaric acid was first obtained by Zinin (*Jahresbericht*, 1877, 813) by fusing amaric acid with caustic potash, and was regarded by him as an ethylbenzylbenzoic acid. Klingemann (*Annalen*, cclxxv., 81) suggested that it might be a diphenylbutyric acid.

Incidentally it was observed that when desyleneacetic acid is boiled with aqueous caustic potash it is hydrolysed, yielding deoxybenzoin. Desylenemalonic acid is stable under these conditions.

67. *Electrolysis of Potassium Allo-ethylic Camphorate. Part II.* By JAMES WALKER, Ph.D., D.Sc., and JAMES HENDERSON, B.Sc.

In addition to the compounds previously described (*Trans.*, 1895, 337) the authors have obtained from the product of electrolysis of potassium allo-ethylic camphorate, a hydrocarbon, C_8H_{14} , boiling at 120°, which is formed by the decomposition of an acid, $\text{C}_9\text{H}_{14}\text{O}_2$, on heating. This hydrocarbon is apparently identical with *lauroleone* prepared from camphanic acid. A ketonic acid, $\text{C}_9\text{H}_{14}\text{O}_3$, m. p. 228°, was also isolated and investigated. The authors conclude that camphoric acid contains the complex $-\text{CH}_2\cdot\text{CH}(\text{COOH})\cdot\text{C}(\text{COOH})-$.

68. "Fluorene and Acenaphthene." By W. R. HODGKINSON.

Some recent communications in the *Annalen*, by Græbe and his students, on fluorene and acenaphthene, necessitate a short notice on my part about these substances in order to maintain priority.

The author has worked at these hydrocarbons and their derivatives for the past twelve years, and in *Proc.*, 1885, 36, reference is made to previous notes on the behaviour of fluorene ($\text{C}_{13}\text{H}_{10}$) when heated alone, in air, or with

oxidising agents. Lately he has associated Mr. A. H. Coote with this work.

In the paper above quoted it is indicated that the red substance obtained from fluorene (and also from acenaphthene) can be separated from the hydrocarbons (there called difluoryls, $C_{26}H_{18} \alpha.\beta.\gamma$), and that this red substance is not a simple hydrocarbon, but contains oxygen.

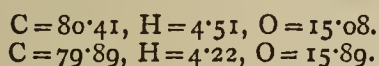
During the past three years a great number of results have been obtained.

One conclusion arrived at is that no red or coloured hydrocarbon is produced by the oxidation of either fluorene or acenaphthene. The coloured compounds produced, along with the doubled molecule in the case of fluorene, $C_{26}H_{18}$ (difluoryl), and the coloured substance along with acenaphthylene in the case of acenaphthene, have been obtained almost pure. It is found that not only on heating with litharge, as Behr and Van Dorp first showed, but that almost any other oxide, and even potash, soda-lime, and chalk Iceland spar, will produce coloured oxidation products from both fluorene and acenaphthene, and especially from the latter. Phenanthrene, naphthalene, and anthracene do not act in the same manner.

On the other hand, both fluorene and acenaphthene may be passed along with hydrogen, steam, or hydrogen chloride, through a red hot platinum tube without change.

The isolation of these oxidation products is a difficult matter. They are not volatile alone without decomposition, and are as soluble in the usual liquids as the hydrocarbons. Picric acid also seems to precipitate them as well as the hydrocarbons.

The ethereal and chloroform solutions of these oxidation products are highly fluorescent. The one from acenaphthene more so than that from fluorene. They form compounds with acid sulphites which are non-fluorescent. Two analyses (preps. 5 and 7) taken at random:—



The coloured substance from fluorene is more difficult to obtain in quantity, or pure. The average percentage of oxygen is between 9 and 10.

Sulphur behaves like oxygen towards both these hydrocarbons, and selenium also to a lesser extent. When the hydrocarbons are heated with dry sodium thio-sulphate, or with some metallic sulphides, sulphur compounds of a red or orange colour are produced. Their solutions in ether and chloroform are also fluorescent. With sulphur or selenium, hydrogen sulphide and selenide are respectively produced. In the case of fluorene a difluoryl is also produced on heating with sulphur.

Several analyses of the red compound from acenaphthene and sulphur indicate the presence of about 13.26 per cent of sulphur.

Research Fund.

A meeting of the Research Fund Committee will be held in June. Applications for grants, accompanied by full particulars, should be sent to the Secretaries before June 8th.

PHYSICAL SOCIETY.

Ordinary Meeting, May 22nd, 1896.

Prof. AYRTON, Vice-President, in the Chair.

MR. R. APPLEYARD read a paper on "Dielectrics."

The author has particularly investigated the effect of temperature on the dielectric resistance. He has employed for this purpose condensers insulated with mica and paraffined paper. In order to eliminate some of the effects of surface leakage, Price's guard-ring arrangement was made use of in all the experiments.

The author finds that the capacity of a paraffin con-

denser varies irregularly with the temperature, but that to within the accuracy attainable with his instruments (1 per cent) the capacity of a mica condenser is constant between 33° F. and 110° F.

If the resistance of paraffin at a temperature t is represented by $R_t = Ra^t$, the mean value for $\log. a$, deduced from all the author's measurements, is $\bar{1} \cdot 96344$.

Experiments made with a parallel plate condenser, with paraffin as the dielectric, show that when the temperature reaches within about 20° of the melting-point the resistance rapidly falls; when melting commences there is a rapid drop, but while melting is in progress the resistance remains constant.

Prof. AYRTON said he could bear witness to the extreme value of Mr. Price's device, as it completely did away with the necessity for the extreme care previously required to prevent errors due to surface leakage. He regretted that he had not had an opportunity of comparing the author's numbers with some obtained some years ago by Prof. Perry and himself (Prof. Ayrton).

A paper by Prof. VIRIAMU JONES, on "*The Magnetic Field due to an Elliptical Current at a point in the Plane of the Ellipse and within it*," was taken as read.

Prof. SILVANUS THOMPSON said that this paper was of interest, not only on account of the application which others might make of the author's method, but also in that the correction, when applied to Prof. Jones's results, brought the international ohm more nearly into accord with the true ohm.

Mr. J. J. WALKER said he considered that the paper was more suited to the Mathematical Society. The integration which the author reduced to elliptic integrals might be more easily performed by another method.

Prof. AYRTON said that Prof. Jones's value for the true ohm was now 106.302 c.m. of mercury.

Mr. CAMPBELL read a paper on "*New Instruments for the Direct Measurement of the Frequency of Alternating or Pulsating Electric Currents*."

The author employs two arrangements, in one of which a steel wire the tension on which is variable, and the other a steel spring of variable length clamped at one end, are acted upon by an electro-magnet through which the periodic current is passed. The tension or length, as the case may be, is varied till maximum resonance is obtained, a small contact piece being employed to detect when this occurs. The instrument exhibited was capable of measuring the frequency of periodic currents of from 40 to 150 double vibrations per second.

Mr. WATSON said he thought that in the case of the spring there would be a considerable temperature correction, and he suggested a method by which this might be compensated.

Mr. BLAKESLEY asked if the author had found that the spring became magnetised, and thus gave the octave.

Mr. CARTER asked whether elastic fatigue influenced the results, and said that a synchronous motor and a speed indicator could be used to measure the frequency.

Prof. SILVANUS THOMPSON suggested that it might be better to employ a polarised apparatus, since, to avoid the impression of forced vibrations on the spring, it was better, as was done in the case of tuning-forks, to make it massive. It had been found in other cases, such as in Hughes's telegraph and the telephone, that better results were obtained with polarised apparatus. He (Prof. Thompson) had used a telephone, placed anywhere near a magnet traversed by the periodic current, together with a tuning-fork, which gave beats with the note produced by the telephone, to measure frequencies. The variations in frequency ordinarily met with in practice were much greater than was generally suspected.

Mr. BLAKESLEY said he considered that the advantage of the author's instrument over a telephone and tuning-fork was that it was continuously variable over a large range.

Mr. ENRIGHT asked if the author had been troubled by

the spring or wire breaking into overtones. In some experiments, in which rather long wires were used, he had been troubled in this way.

Prof. AYRTON said that he did not think that it was possible to get the wire or spring to respond to the octave unless the alternating current contained a component of the frequency of the octave. In fact, he had himself used such a stretched string as a wave analyser. He had used a telephone to prove that the note given by a hissing alternate current arc corresponded in frequency to that of the current. In the instrument used by Prof. Perry and himself a polarised arrangement was always employed, since the alternating current was passed either through a wire in a constant magnetic field, or through an electromagnet which acted on a wire through which a constant current was passed.

The Author, in his reply, said that the instrument responded, though feebly, to the octave, and this response might be made use of to check the accuracy of the scale.

The Society then adjourned till June 12th.

NOTICES OF BOOKS.

Synopsis of Current Electrical Literature: compiled from [fifty-nine American and Foreign] Technical Journals and Magazines during 1895. By MAX OSTERBERG. *Electric Power*, 27, Thames Street, New York; D. van Nostrand Co., 23, Murray Street, New York. 1896. Pp. xiii.—143, 8vo.

WHILE the Royal Society is making plans for indexing scientific literature of the next century on a grand scale, the Office International de Bibliographie, at Brussels, is stimulating the efforts of the French-speaking people, and the Bureau of Zoological Literature established by Dr. Field at Zurich is furnishing a centre of influence for the whole world of zoologists, the Americans are pushing forward in the same lines. The bibliographical publications of the Smithsonian Institution are well known and highly valued; the superb Index-Catalogue of the Medical Library of the U.S. Army, successfully concluded last year by its distinguished director, Dr. John S. Billings, furnishes the highest model of excellence to all librarians; the labours of the Committee on Indexing Chemical Literature of the American Association for the Advancement of Science, now in its fourteenth year of activity, are well known through its reports annually published in the CHEMICAL NEWS. Besides these concerted efforts, individual enterprise in America is accomplishing much good work of a kindred nature: of such is the volume now under review. Mr. Osterberg's Monthly Journal, *Electric Power*, offers its readers Synopses of current electrical literature, and this material re-arranged in convenient form constitutes this annual volume.

The compiler states that the principal aim has been to give the "headings and names of authors of the most important articles pertaining to electricity published in the English, German, and French languages during the past year." This has certainly been accomplished; the titles are followed by brief comments characterising the article cited. The titles are grouped under the sixteen following heads:—

Alternating Currents; Biographical; Central Stations; Dynamos and Motors; Educational; Electro-chemistry; Electro-physics; Electro-therapeutics; Isolated Plants; Lighting (Arcs, &c.); Magnetism: Measurements and Instruments for Measuring; Railways; Storage Batteries; Telegraphy, Telephony, &c.; Transmission and Power.

There is an author index. The book will prove invaluable to every electrician who desires to keep abreast of the times.

Handbook for the Biochemical Laboratory, including Methods of Preparation and numerous Tests, arranged Alphabetically. By JOHN A. MANDEL, Professor of Chemistry at the New York College of Veterinary Surgeons, and Assistant to the Chair of Chemistry at the Belle Vue Hospital Medical College and the College of the City of New York. First Edition. First Thousand. New York: J. Wiley and Sons. London: Chapman and Hall, Ltd. 1896.

THE American press is at present fairly fruitful in chemical publications, and not so much in sketchy pamphlets and "manualettes," written in accordance with the latest syllabus, one of them differing from another barely enough to satisfy the law of copyright as in sound publications. The work before us will be unquestionably useful to the chemical student, to the praktikant,—an English word is here wanting,—and to the physician. We find here, firstly, directions for preparing in a state of purity the most important fluids and tissues which enter into the composition of the animal body.

Then follow tests for the animal constituents, in number exceeding two hundred. We must of course admit, if that be any fault, that there is here no little which will grind the gentle spirit of Victoria Street

"Into a powdery foam of salt abuse,
Ruffling the ocean of their self content."

But none the less do we wish Mr. Mandel's work good speed and a large circulation.

Handbook of Chemical Technology. ("Handbuch der Chemischen Technologie"). Elaborated in association with several Savants and Technicians. Edited by Dr. P. A. BOLLEY and Dr. K. BIRNBAUM. Continued, after the death of the Editors, by Dr. C. ENGLER, Privy Aulic Councillor and Professor of Chemistry at the Technical High School of Carlsruhe. Eight Volumes, mostly divided into several groups. First Volume—Third Group: Chemical Technology of Fuel. By Prof. Dr. FERDINAND FISCHER, of Göttingen. With numerous Woodcuts in the Text. London, Edinburgh, and Oxford: Williams and Norgate. 1896.

AFTER a brief section on the liberation of heat in and by chemical action, the author passes in review the principal kinds of fuel. As regards wood, we learn that amongst the European countries, England—probably Britain—has the lowest percentage of land occupied by woods, namely 4.0, whilst Denmark has 4.8 and Portugal 5.3. This circumstance we may remark is due to local taxation.

In some kinds of timber the proportion of moisture reaches, or even exceeds, 50 per cent. The proportion of ash in heart-wood is highest in the horse-chestnut, 2.8 per cent; in the oak and the beech, 0.5, and in the firs as low as 0.21. Under some circumstances more phosphorus may be introduced into iron during smelting with charcoal than with coke. The average amount of phosphorus in the beech charcoal is 0.1485 per cent, and in coke from Ostrau only 0.024 to 0.052.

Peat or turf has been in use as a domestic source of heat from the time of Pliny. The chief agents in its formation are the heaths *Calluna vulgaris* and *Erica tetralix*, the mosses, such as *Sphagnum* and *Hyphnum* (species), and a variety of other plants, the separate functions of which in the formation of peat is not completely understood. The utilisation of heat by pressing and exsiccation has been the subject of many inventions, none of which seem to have given complete satisfaction. Hence the use of peat is chiefly confined to localities where coal and wood are not easily procurable. Certain peats—i.e., those of Berks, Hants, &c.—have a destructive influence upon vegetation due to the presence of ferrous sulphide and possibly arsenide (?).

Coal has now for a long time taken the lead among fuels, at least for industrial purposes. Its use may be

traced back to a high antiquity. According to Lyell, coal must have been used in Scotland some 5000 years ago. There is evidence that the Romans made use of coal at their settlements in England. Pliny and Vitruvius, remarkably enough, make no mention of this fact. Coal-mining at Zwickau can be traced back to the tenth century, and by the year 1348 their combustion was found to be a nuisance. Coal-smoke was even said to have occasioned the plague! Legislation against coal-smoke was initiated in England in the reign of Edward I., but proved a complete failure, as did the subsequent enactments of Queen Elizabeth.

The coal-deposits of China are, on the authority of Von Richthofen, estimated as the most important of the entire globe. The coal-beds of Natal and the adjoining parts of the Orange Free State have been overlooked in this survey, though they are reputed as being more valuable than those of Britain, even before they had begun to be worked.

The warning is given that the earth's supply of coal, though vast, is by no means inexhaustible, and that with its end the present culture of Europe must cease. Hence the existing stores should be used judiciously.

The ash of coal often contains phosphoric acid, according to Le Chatelier, in quantities up to 3 per cent. The ash of Westphalian coal, according to Platz, contains as much as 0.5 per cent of copper, lead, and zinc. Arsenic is also not absent, appearing in the form of arsenical pyrites. Coal and soot contain from 0.89 to 0.117 per cent of arsenious acid. Nickel, thallium, and lithium are also occasionally present. Some coals contain barium sulphate.

The subject of explosions in coal-mines and coal-magazines is very fully discussed. The loss of life in the chief States of Europe from 1871 to 1880 is given at no fewer than 4471 men, more than the half of this loss—2686 men—being the share of Britain. But the coal industry in the same decennium and in the same countries cost altogether the lives of 21,256 men, King Coal having demanded the sacrifice of 16,785 lives in other manners. It is here rightly held that, in spite of the best ventilation, the use of good safety lamps and suitable blasting materials is of the utmost importance. The authors seem scarcely to ascribe sufficient importance to the part played in the explosions by coal-dust.

Nearly connected with this subject is the so-called spontaneous ignition of coal on ship-board, in magazines, &c. The majority of experts think now that ventilation is no safe remedy. Of 70 coal-ships lost by spontaneous combustion in 1874, it is certain that 38 were ventilated, whilst the contrary is not reported of any of the rest. Smalls and moist lots are generally condemned, as is also highly pyritiferous coal, especially if the pyrites is present not in lumps, but in minute quantities.

A proposal of the highest value—if not too expensive—is to place, among the coal in the hold, bottles containing compressed carbon dioxide, and closed with stoppers fusible at certain temperatures.

It is generally recognised that the danger of spontaneous ignition on board ship increases with the quantity of coal. A vessel carrying 500 tons of coal is rarely in peril of fire, whilst cargoes of 1500 to 2000 tons have often been destroyed by fire. It is recommended that coal should not be shipped very fresh from the mine.

Action of Hydrobromic Gas upon Thiophosphoryl Chloride.—A. Besson.—The compound resulting, PSCl_2Br , distils at 80° under a reduced pressure. Under the action of cold it becomes a white solid body fusible at -30° . At 0° its sp. gr. = 2.12. In contact with cold water it is slowly decomposed, but more quickly by an alkaline or ammoniacal solution, with liberation of sulphur. In contact with fuming nitric acid there is a violent reaction, which is much less violent with acid at 36° , when the sulphur and phosphorus are converted into sulphuric and phosphoric acids.—*Comptes Rendus*, cxxii., No. 19.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 18, May 4, 1896.

Electrostatic Deflection of the Kathodic Rays.—G. Jaumann.—(In reply to H. Poincaré).—These feeble rays are very strongly deflected by electrostatic rays. A rod of glass rubbed and agitated at the distance of 50 c.m. from the tube deflects the rays. A rod of ebonite deflects them in a contrary direction. Charged conductors deflect them in corresponding directions.

Apparatus for the Measurement of Currents of High Frequency.—G. Gaiffe and E. Meylan.—The author discusses the thermic galvanometer and the induction ammeter.

Reply to the Observations of Auguste Righi.—L. Benoist and D. Hurmuzescu.—The authors consider that it results from their experiments, as well as from those of Righi, that the action of the X rays upon an electrified body is the total dissipation of its electricity, as if the conductor were in connection with the earth. Now, in cases where there exist electromotive contact forces, the conduction to earth causes exactly the existence of an electrification of the magnitude of one volt.

Relation between the Maximum Production of X Rays, the Degree of the Vacuum, and the Form of the Tubes.—Victor Chabaud and D. Hurmuzescu.—This paper cannot be inserted without the accompanying woodcuts.

Radiographs. Applications to the Physiology of Movement.—A. Imbert and H. Bertin-Sans.—After the radiographs of the wrist, the elbow, and the knee, which we have had the honour of submitting to the Academy, we have obtained analogous results for the shoulder, the tarsus, and the lumbar region of the vertebral column. All these proofs have been obtained from the living subject.

Transformation of Tariric Acid and of Stearoleic Acid into Stearic Acid.—A. Arnaud.—The tariric acid which the author discovered some years ago in the seeds of the Tarin of Guatemala (*Picramnia*, sp. α of the *Simarubicæ*) is a crystalline fatty acid belonging to the non-saturated crystalline series, $\text{C}_n\text{H}_{2n-4}\text{O}_2$. It is isomeric with stearoleic acid. Tariric acid belongs to the oleic-stearic group.

Presence in *Monotropa hypopithys* of a Glucoside of the Methylsalicylic Ether, and on the Hydrolysing Ferment of this Glucoside.—Em. Bourquelot.—It results from all the facts adduced that one and the same hydrolysing ferment of gaultheria exists in the roots of *Spirea ulmaria*, *filipendula*, and *salicifolia*; in the root of *Polygala*; in the bark of *Betula lenta*; in the leaves and the fruits of *Gaultheria procumbens*; and in the petals of *Azalea*. There exists in *Monotropa hypopithys* a glucoside which is hydrolysed by this ferment, and which is in consequence probably identical with gaultherine. This ferment is probably peculiar, for neither gaultherine nor the glucoside of *Monotropa* are hydrolysed by this ferment, and the ferment which acts upon these glucosides has no action upon others.

Maize.—M. Balland.—Maize contains as much nitrogen and phosphatic ash as the average of French wheats, and three or four times more fatty matter. Hence it is a more complete food than wheat.

Fermentation of Uric Acid by Micro-organisms.—E. Gérard.—Uric acid is decomposed by the action of micro-organisms into urea and ammonium carbonate. It

is very probable that the urea, the principal product formed, is subsequently subject to the action of an urophagous microbe when it is hydrated, yielding ammonium carbonate.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. i., No. 1.

Report by P. Bérard on two Respiratory Appliances by Drs. Detourbe and Détröye.—The Committee of Chemical Arts has awarded a premium to the mask constructed by Dr. Détröye, but at the same time they render full justice to the apparatus presented by M. Detourbe. These respirators cannot be described without the accompanying figure.

The Industrial Work of Pasteur.—E. Duclaux.—The writer gives an account of Pasteur's successful attempt to conquer the silk-worm disease and his studies on fermentation. Incidentally, reference is made to the grand principle of attenuation, by means of which the extirpation of various diseases of mankind are in course of being overcome. By a curious coincidence the paper was read on the anniversary of Pasteur's birthday.

Improvements in the Manufacture of Hydrochloric Acid and of Bleaching Products.—M. Buisine.—The author gives an especial account of the ammonia-soda process, which he considers as at present predominant, though the electrolytic procedures are attracting much attention.

Among the "Chemical Notes" is mention of a case of so-called spontaneous combustion in certain red leads which have been brightened with eosine.

No. 2, 1896.

This number contains no chemical matter.

MEETINGS FOR THE WEEK.

MONDAY, June 1st.—Society of Chemical Industry, 8. "Japanese Metallurgy—Part I. Gold and Silver and their Alloys," by W. Gowland, F.I.C. "Electro-deposition of Zinc," by Sherard Cowper-Coles.

TUESDAY, 2nd.—Royal Institution, 3. "The Building and Sculpture of Western Europe," by Prof. T. G. Bonney, F.R.S.

— Institute of Civil Engineers, 8. (Anniversary).

WEDNESDAY, 3rd.—Royal Institution, 3. "Vault of the Sixtine Chapel," by Prof. W. B. Richmond, R.A.

— Society of Public Analysts, 8.

THURSDAY, 4th.—Royal, 4.30.

— Royal Institution, 3. "Lake Dwellings," by R. Munro, M.D., M.A.

— Chemical, 8. "The Magnetic Rotation of Organic Substances, with especial reference to Benzenoid Compounds," by Dr. W. H. Perkin, F.R.S.

FRIDAY, 5th.—Royal Institution, 9. "Electric and Magnetic Research at Low Temperatures," by Prof. J. A. Fleming.

— Geologists' Association, 8.

— Quekett Club, 8.

SATURDAY, 6th.—Royal Institution, 3. "The Moral and Religious Literature of Ancient Egypt," by Dr. E. A. Wallis Budge, M.A.

THE X-RAYS.

New Work by Wm. ACKROYD, F.I.C., &c.

THE OLD LIGHT AND THE NEW: Dealing with the Chemistry of Colour and the New Photography. Price 1s. 6d. net.

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CITY AND GUILDS OF LONDON INSTITUTE.

SESSION 1896-97.

The Courses of Instruction in ENGINEERING and CHEMISTRY at the Institute's Colleges commence in October, and cover a period of two to three years. The MATRICULATION EXAMINATION of the CENTRAL TECHNICAL COLLEGE will be held on September 21st to 24th, and the ENTRANCE EXAMINATION of the Day Department of the TECHNICAL COLLEGE, FINSBURY, on September 22nd.

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(Exhibition Road, S.W.), a College for higher Technical Instruction for students not under 16 years of age preparing to become Civil, Mechanical, or Electrical Engineers. Chemical and other Manufacturers, and Teachers.

THE MATRICULATION EXAMINATION will be held on September 21st to 24th, and the new Session will commence on October 1st.

Professors:—O. HENRICI, LL.D., F.R.S. (Mathematics), W. C. UNWIN, F.R.S., M.I.C.E. (Civil and Mechanical Engineering), W. E. AYRTON, F.R.S. (Physics and Electrical Engineering), H. E. ARMSTRONG, Ph.D., F.R.S. (Chemistry).

CITY AND GUILDS TECHNICAL COLLEGE, Finsbury (Leonard Street, City Road, E.C.). The DAY DEPARTMENT provides Courses of Intermediate Instruction for Students not under 14 years of age, preparing to enter Mechanical or Electrical Engineering and Chemical Industries.

THE ENTRANCE EXAMINATION will be held on September 22nd, and the new Session will commence on October 6th.

Professors:—S. P. THOMPSON, D.Sc., F.R.S. (Electrical Engineering), J. PERRY, D.Sc., F.R.S. (Mechanical Engineering), R. MELDOLA, F.R.S. (Chemistry).

JOHN WATNEY,
Hon. Secretary.

City and Guilds of London Institute,
Gresham College, Basinghall Street, E.C.

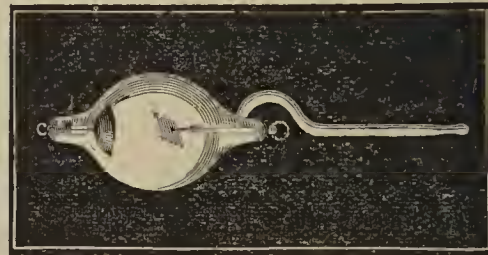
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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1906.

HELIUM AND ARGON.

PART III.—EXPERIMENTS WHICH HAVE YIELDED NEGATIVE RESULTS.*

By WILLIAM RAMSAY, Ph.D., F.R.S., and J. NORMAN
COLLIE, Ph.D., F.R.S.E.

To chronicle a list of failures is not an agreeable task; and yet it is sometimes necessary, in order that the record of the behaviour of newly-discovered substances may be a complete one. It is with this object that we place on record an account of a number of experiments made to test the possibility of forming compounds of helium and argon.

It will be remembered that, in our memoir on Argon (*Phil. Trans.*, vol. clxxxvi., A), Lord Rayleigh and Prof. Ramsay described numerous experiments, made in the hope of inducing argon to combine, all of which yielded negative results. Two further experiments have been since made—again without success.

1. The electric arc was maintained for several hours in an atmosphere of argon. The electrodes were thin pencils of gas carbon, and, previous to the introduction of the argon, the arc was made in a vacuum, and all gas evolved was removed by pumping. Argon was then admitted up to a known pressure, and the arc was again made. A slow expansion took place; one of the electrodes diminished in length, and the bulb became coated with a black deposit. The resulting gas was treated with caustic soda and with a solution of ammoniacal cuprous chloride, and, on transference to a vacuum-tube, it showed the spectrum of argon along with a spectrum resembling that of hydrocarbons. Having to leave off work at this stage, a short note was sent to the *CHEMICAL NEWS* on a "Possible Compound of Argon." On resuming work after the holidays, the gas was again investigated, and, on sparking with oxygen, carbon dioxide was produced. But it was thought right again to treat the gas with cuprous chloride in presence of ammonia, and it now appeared that, when left for a sufficient time in contact with a strong solution, considerable contraction took place, carbonic oxide being removed. There can, therefore, be no doubt that, although apparently all gas had been removed from the carbon electrodes before admitting argon, some carbon dioxide must have been still occluded, probably in the upper part of the electrodes, and that the prolonged heating due to the arc had expelled this gas and converted it into monoxide. It was, indeed, inexplicable how an expansion should have taken place unless by some such means; for the combination of a monatomic gas must necessarily be accompanied by contraction. It appears, therefore, certain that argon and carbon do not combine, even at the high temperature of the arc, where any product would have a chance of escaping decomposition by removing itself from the source of heat. It is hardly necessary to point out that such a process lends itself to the formation of endothermic compounds such as acetylene, and it was to be supposed that, if argon is capable of combination at all, the resulting compound must be produced by an endothermic reaction.

2. A product rich in barium cyanide was made by the action of producer gas on a mixture of barium carbonate and carbon at the intense temperature of the arc. This product was treated by Dumas's process so as to recover all nitrogen; and, as argon might also have entered into combination, the nitrogen was absorbed by sparking. All

the nitrogen entered into combination with oxygen and soda, leaving no residue. Hence it may be concluded that no argon enters into combination. For the successful carrying out of these experiments we have to thank Mr. G. W. MacDonald.

3. A mixture of argon with the vapour of carbon tetrachloride was exposed for several hours to a silent discharge from a very powerful induction coil. The apparatus was connected with a gauge which registered the pressure of the vapour of the tetrachloride and of the argon of which it was mixed. Careful measurement of the pressure was made before commencing the experiment and after its completion. Although a considerable amount of other chlorides of carbon was produced, no alteration of pressure was noticeable, the liberated chlorine having been absorbed by the mercury present. Here again the argon did not enter into the reaction, but it was recovered without loss of volume.

The remaining experiments relate to attempts to produce compounds of helium. The plan of operation was to circulate helium over the reagent at a bright red heat, and to observe whether any alteration in volume occurred—an absorption of a few c.c. could have been observed—or whether any marked change was produced in the reagent employed. As a rule, after the reagent had been allowed to cool in the gas, all helium was removed with the pump, and the reagent was again heated to redness, so as, if a compound had been formed, to decompose it and expel the helium. Every experiment gave negative results; in no case was there any reason to suspect that helium had entered into combination.

A short catalogue of the substances tried may be given.

4. Sodium distilled in the current of gas, and condensed in drops with bright metallic lustre. The glass tube in which it was heated became covered with a coating of—

5. Silicon, which caused no absorption.

6. A mixture of beryllium oxide and magnesium, yielding metallic beryllium, was without action.

7. Zinc, and 8, cadmium, distilled over in the current of gas.

9. A mixture of boron oxide and magnesium dust, giving elemental boron, produced no absorption.

10. Similarly, a mixture of yttrium oxide and magnesium dust had no effect.

11. Thallium was heated to bright redness in the gas, retaining its metallic lustre.

12. Titanium oxide mixed with magnesium dust was heated to bright redness, and caused no absorption.

13. Similar absence of action was proved with thorium oxide and magnesium powder.

14. Tin, and 15, lead, were heated to bright redness in the current of gas, and remained untarnished.

16. Phosphorus was distilled in the gas, and caused to pass through a length of combustion-tube heated to softening. Some red phosphorus was formed, but no alteration of volume was noticed.

17. The same process was repeated with elemental arsenic.

18. Antimony, and 19, bismuth, at a bright red heat, retained their metallic lustre.

20. Sulphur, and 21, selenium, were treated in the same way as phosphorus; no action took place.

22. Uranium oxide, mixed with magnesium dust, was heated to bright redness in helium. No change, except the reduction of the oxide, took place. The mixture was allowed to cool slowly in the current, and the helium was removed with the pump till a phosphorescent vacuum was produced in a vacuum tube communicating with the circuit. The mixture was re-heated, and no helium was evolved—not even enough to show a spectrum. The vacuum remained unimpaired.

It had been hoped that elements with high atomic weight, such as thallium, lead, bismuth, thorium, and uranium, might have effected combination, but the hope was vain,

* A Paper read before the Royal Society, May 21, 1896.

23. A mixture of helium with its own volume of chlorine was exposed to a silent discharge for several hours. The chlorine was contained in a reservoir, sealed on to the little apparatus which had the form of an ozone apparatus. No change in level of the sulphuric acid confining the chlorine was detected after the temperature, raised by the discharge, had again become the same as that of the room. Hence helium and chlorine do not combine.

24. Metallic cobalt in powder does not absorb helium at a red heat.

25. Platinum black does not occlude it.

26. It is not caused to combine by passage over a mixture of soda-lime and potassium nitrate heated to bright redness. This was hardly to be expected, for it resists the action of oxygen in presence of caustic soda, even when heated by the sparks which traverse it.

27. A mixture of soda-lime and sulphur consisting of polysulphides causes no change of volume in a current of helium passed over it at a bright red heat.

28. Induction sparks in an ozone apparatus passed through a mixture of helium with benzene vapour in presence of liquid benzene for many hours, gave no change of volume. The benzene was, of course, altered, but the sum of the pressures of the helium and the benzene vapour remained as at first. Had helium been removed, contraction would have occurred.

This ends the catalogue of negative experiments. Any compound of helium capable of existence will probably be endothermic, and the two methods of producing endothermic compounds, where no simultaneous exothermic reaction is possible, are exposure to a high temperature, at which endothermic compounds show greater stability, and the influence of the silent electric discharge. These methods have been tried, so far in vain. There is, therefore, every reason to believe that the elements, helium and argon, are non-valent, that is, are incapable of forming compounds.

ON THE COLOUR RELATIONS OF ATOMS, IONS, AND MOLECULES.

PART II.

By M. CAREY LEA.

I.—Interaction of Ions.

IF a coloured substance be formed by the union of a colourless kation with a colourless anion, the colour belongs to the molecule only. The colourless ions have so modified each others' vibration periods that selective absorption is exercised. As soon, therefore, as the molecule is divided into ions the colour must disappear. Consequently, if we find a solvent which, like water, is capable of separating the ions, the resulting solution, when dilute, must be colourless, no matter how intense the colour of the compound.

The truth of this law of interaction has been tested experimentally in a considerable number of cases. The results, which were found to be without exception confirmatory, are given below.

Alkaline Metals.—These form comparatively few coloured products, soluble in water, by uniting with colourless atoms. Well marked instances are, however, found in the monosulphides.

Potassium sulphide, K_2S , is in the solid form cinnabar-red. It dissolves in water to a colourless solution.* The sodium salt acts similarly. As to the alkaline selenides and tellurides, their tendency to form poly-salts is so great that it is not possible to judge of the colour shown by mono-salts in solution. It is of interest, however, that

hydrogen selenide, and probably, also, the tellurides, are colourless; also, the oxygen acids of both are colourless. There is little doubt, therefore, that selenium and tellurium, like sulphur, have colourless ions.

Mercuric iodide affords an excellent illustration of the principle stated, owing to the large variety of solvents for it.

In hot ethylic alcohol it dissolves easily. Solution absolutely colourless; gives a cloud when poured into water, which settles to a red powder.

Methylic alcohol acts similarly.

In solution of calcium chloride, especially if hot, dissolves easily; less easily in barium chloride.

In solution of potassium and sodium chlorides, dissolves sparingly. All these solutions are colourless.

In solutions of potassium bromide, and of iodide, it dissolves abundantly. Strong solutions have a yellowish colour, but become colourless by moderate dilution. These two salt solutions dissolve mercuric iodide freely in the cold; the other solvents need heat.

In cold solution of mercuric nitrate, it dissolves easily to a colourless solution. In solution of mercuric chloride it is somewhat soluble; the solution is colourless.

In glycerin it dissolves pretty well with the aid of heat, and does not communicate a trace of colour.

Mercuric arsenite is bluish grey. It is slightly soluble in solution of sodium arsenite. The solution is colourless.

Mercuric arsenate is pale yellow. It dissolves in a solution of mercuric nitrate, and also in one of sodium pyrophosphate; both solutions are colourless.

The black heavy metallic sulphides are very difficult substances to bring into solution, but it seems that when this can be done the solution is colourless when the ions are colourless. This can be shown to be the case with mercuric sulphide and with antimonious sulphide. According to Weber (*cf.* "Gmelin-Kraut," iv., p. 851), when mercuric chloride is precipitated with an excess of ammonium sulphide, the precipitate dissolves in potash to a colourless solution.

Silver oxide is slightly soluble in water. Being very deeply coloured, it would seem natural that its solution should show this colour; but the solution is absolutely colourless. This is because the silver ion is colourless. Metallic oxides having coloured ions carry that colour into their solutions, as is seen in the case of cupric oxide in alkaline solutions, and in soluble forms of ferric oxide.

Silver arsenite is lemon-yellow; it is abundantly soluble in ammonia-water and in mercuric nitrate. Both solutions are colourless.

Silver Arsenate.—Chocolate colour; dissolves in the same solvents as the last, and also gives colourless solutions.

Silver Phosphate.—Triargentic phosphate dissolves with facility in nitric acid, in ammonia-water, and in mercuric nitrate. All three solutions are colourless.

Cuprous Sulphite (Gmelin, "Handbook," Ger. ed. iv., p. 622).—Red; dissolves in ammonia-water and in dilute hydrochloric acid, giving colourless solutions.

Stannic Sulphide, precipitated.—Ochre-yellow; dissolves in warm potash or soda solution; the resulting solution is nearly colourless.

It also dissolves in potassium sulpharsenite to a colourless solution.

Red antimony pentasulphide dissolves in alkaline monosulphides; solutions colourless.

Orpiment (As_2S_3) dissolves easily in warm potash or soda solution; colourless.

2.—Combinations of Ions.

Ions may combine:—A. Two or more similar colourless ions may unite to form a coloured elementary molecule.

The ions of iodine and bromine are colourless, as shown in solutions of HBr and KBr , HI and KI . The molecules are strongly coloured. The ions of lead are colourless, as shown in solutions of lead nitrate or acetate.

* Graham Otto, 5th Ger. ed., vol. iii., p. 240. The reactions here described have been either found or verified by the writer, except in a few instances, and in these, as in the present case, the authority on which they are stated is given.

The molecule (or the polymer) of lead is blue. The ion of sulphur is colourless—water is not coloured when saturated with sulphydric acid. The oxygen acids of sulphur are colourless; but the molecule is yellow. Selenium has a colourless ion, but a strongly coloured molecule. Colourless cuprous ions unite to form red copper.

B. Two or more similar ions, coloured, may unite to form a colourless (or white) molecule, or polymer. The ion of platinum is yellow in Pt^{IV} , red in Pt^{II} ; in each case the ions unite to form white platinum. The nickel ion is green; these unite to form white metallic nickel.

C. Two or more similar ions, coloured, may unite to form a molecule of a wholly different colour. Blue copper ions may unite to form red copper.

D. Two or more dissimilar colourless ions may unite to form a coloured molecule. Sulphur and nitrogen unite to form orange-coloured nitrogen sulphide. Sulphur and silver to form black silver sulphide.

It is an interesting fact, and one I believe that has not been previously noticed, that no ion, and therefore no atom, is black, but is always transparent to some portion or portions of the visible rays. In this respect atoms and ions differ absolutely from molecules. For these last are often black, and this may be the case even with elements—as, for example, iodine in the solid form, platinum black, &c. The absolute difference between atoms and molecules, the entire absence of colour relation between them, was mentioned in the first part of this paper; it must always be one of the most remarkable facts in chemistry.

The production of a black molecule in no way depends upon the combination of two or more atoms having different relations to light, such that one should extinguish the rays which the other or others allow to pass. This might almost be expected, but is far from being the case. Two colourless atoms may unite to form a black molecule, as in the cases just mentioned.

It seems scarcely necessary to say that these remarks relate to inorganic molecules only. For in organic molecules, chemical composition has little influence; isomeric combinations exhibit the greatest differences, and their spectra show little relation to those of their elements (Ostwald, "Lehrb.," 2nd Ger. ed., i., 472).

With organic compounds, which are formed almost exclusively of colourless atoms, it is always the colour of the molecule that is important. With inorganic compounds the reverse is the case—we have much less to learn from the colour of the molecule; that of the atom is all important. One and the same molecule may present various colours, absolutely unlike each other. Phosphorus and sulphur may be black, red, or yellow. Gold is yellow by reflected, blue or green by transmitted light, and may be red when in a state of fine division. Who shall say in either case which of these colours is characteristic? With the ion, and therefore with the atom, there is no such ambiguity. Its colour, its absorption-spectrum, are invariable; these are always highly characteristic.

3.—Acid Indicators : Theory of their Reactions.

Acid indicators are such as show a striking change by the addition of an alkaline solution; either from one colour to another, or from a colourless to a strongly coloured solution. They may be considered as of the nature of weak acids. Their reactions have been explained (Ostwald, "Lehrbuch," 2nd Ger. ed., i., 800) in this way: that the radicle has, as an ion, a colour different from that which it has in the undissociated compound.

This explanation is unsatisfactory, for two reasons:—

1. It makes the colour of an acid indicator, in presence of an alkali, depend on dissociation. But it can be shown that such a coloured solution may be evaporated to dryness and thoroughly desiccated at 100° without losing anything of the intensity of its colour; that is, the

colour persists under conditions in which dissociation is impossible.

2. It makes the colour—or absence of colour, as the case may be—of the solution of the acid indicator, when isolated, depend upon the absence of dissociation. But it is a familiar fact that, by sufficient dilution, even the weakest acids are largely or even completely dissociated. (All their molecules become active: Ostwald, "Lehrb.," 2nd Ger. ed., ii., 653; Nernst, "The. Ch.," 440).

Let us take litmus for example. This is a weak acid red dye-stuff, which in contact with an alkali becomes blue. According to the explanation here criticised, isolated red litmus has a blue ion, which does not appear in solution because not dissociated. But it is certain that, with sufficient dilution, it must be dissociated; and, according to this explanation, it should then turn blue. Whereas, red litmus remains red by any amount of dilution, so long as any trace of colour is left.

Again, it is said that blue litmus owes its blue colour to dissociation. But the blue solution may be evaporated and desiccated at 100° without losing its blue colour. The colour is, therefore, *not due to dissociation*.

With these complex and faintly acid organic substances it seems probable that some change in their constitution takes place in the presence of an alkali; such that the anion that separates from the dilute solution of the isolated substance is not the same as that which separates from the alkaline combination; that is to say, the anion which separates from red litmus is not absolutely the same as that which separates from blue. Only in this way can the various reactions of acid indicators be satisfactorily explained.

The reactions of these substances have not been studied with sufficient accuracy to indicate exactly what is the change that takes place in the presence of an alkali. It may be either a re-arrangement of some of the atoms, or it may depend on the taking up of one or more molecules of water.

When an alcoholic solution of phenolphthalein is dropped into much water, the resulting solution cannot be distinguished from pure water by its colour. The addition of a trace of potash brings it to a deep rose red. Phenolphthalein acts as a very weak acid; its very dilute solution must therefore be dissociated, and the colourless anion of the isolated substance must differ from the coloured anion which separates from the potash compound.

Also, a solution of the potash compound, so dilute as to leave a transparent film, has been evaporated and then desiccated for many hours at 100° , the colour of the solution still fully remaining in the dry product. Now, the potash compound of phenolphthalein is known to be anhydrous. Anhydrous substances thoroughly desiccated cannot be in a dissociated state, and therefore the rose-red colour of the potash compound is not due to dissociation.

Further, if to the potash solution a solution of a silver salt is added, there is formed a silver compound having the same constitution as that of the potassium compound. This silver compound is anhydrous and insoluble; nevertheless, it has the same colour as the potassium compound under conditions which make dissociation to be out of the question.

Paranitrophenol.—This is another acid indicator. In a solid state it is nearly colourless; it dissolves in warm water to a nearly colourless solution, which, on the addition of an alkali, becomes gold-yellow. A portion of this solution, evaporated so as to leave a thin film, exhibits the same intensity of colour as the solution, which colour it retains after thorough desiccation. The colour of the solution is therefore not due to dissociation. The solution of the substance itself, when largely diluted, gives no indication of the dissociation of a coloured ion. The behaviour of phenacetoline, another acid indicator, is analogous.

It seems, therefore, that dissociation has no essential connection with the reactions of acid indicators. It is

simply that these substances, by combining with alkalis, either have their colour much intensified, or in some cases change it altogether.

Such changes are not in any way confined to acid indicators, so-called. Picric acid, in combining with alkalis, has its colour much intensified; the acid itself has a pale yellow colour; the sodium salt (dry) has a pure deep yellow colour. Chrysammic acid affords an example of a complete change of colour; the acid itself is yellow, the potash salt a deep blood red, not only in solution, but in the dry state, so that its colour cannot be due to dissociation. It may be remarked, also, that the potash salt in its dry state has remarkable optical properties, which were investigated by Brewster—properties not possessed by the acid.

To the reactions which have been here examined might be added those of methyl-orange, rosolic acid, and other acid indicators. I have found no exception to the rule that the characteristic colours exhibited by these substances, when placed in contact with alkalis, are retained after a thorough desiccation. Also, no acid indicator, when dissociated by a large dilution, shows any tendency to exhibit an anion similar in colour to that of its alkaline compound.

(To be continued).

ON THE EXISTENCE OF CUPRIC SULPHIDE.

By JOHN B. COPPOCK, Harris Institute, Preston.

PROF. MENSCHUTKIN has told us, in his "Analytical Chemistry," that the black precipitate obtained by treating cupric solutions with hydrogen sulphide is Cu_4S_3 , and not CuS , this substance being entirely unknown.

Whether the substance which comes down with hydrogen sulphide is Cu_4S_3 is under investigation, but, as a result of the following investigations, it may be definitely said that cupric sulphide has been prepared, and can always be, by the interaction of a copper salt and hydrogen sulphide, particularly when the copper salt is in excess.

As copper forms such a well-defined cupric oxide, it seemed theoretically certain that such a compound as cupric sulphide should be in existence, knowing the relations of sulphur and oxygen.

Copper sulphate was weighed out in the two following quantities,

0.858 grm. and 0.975 grm.,

and dissolved in water, with the addition of a slight amount of hydrochloric acid, as in qualitative work; hydrogen sulphide was passed to saturate the solution. The precipitate was dried under conditions liable to keep the oxidation of the sulphide to sulphate at a minimum.

Theoretically the two quantities above should give—

0.327 grm. and 0.372 grm.

of CuS ; the precipitates actually weighed—

0.350 grm. and 0.386 grm.

What was the error due to? To the existence in each precipitate of free sulphur, which, when the precipitate was ignited after the final weighing, made itself obvious by burning to sulphur dioxide. This free sulphur was due to the action, as is well known, of the acid solution upon the hydrogen sulphide. In every trial this method gave a precipitate which was polluted with free sulphur, and therefore prevented the preparation of a pure precipitate, whether it was Cu_4S_3 or CuS which came down. The following method was therefore adopted:—Hydrogen sulphide was passed into water; the amount passed in was determined; into this solution a known weight of copper sulphate was put, the weight being more than sufficient to combine with the hydrogen sulphide. There-

fore the solution was saturated with the copper salt. This solution had no added acid, so as to prevent the liberation of free sulphur,—so the only acid present was that due to the liberation of sulphuric by the action going on.

Copper sulphate was thus weighed and added as above.

2.4840 grms.

1.8945 grms.

Each placed in the solutions of hydrogen sulphide containing the following amounts:—

0.1100 grm.

0.1100 grm.

The cupric sulphide thus obtained was certainly a little darker than that obtained by the previous method. The precipitate dried at 100° and with no oxidation weighed—

0.3075 grm. and 0.3076 grm.

These facts were sufficient to show that under these conditions CuS had been prepared.

Turning the CuS into its copper sulphate equivalent, we get—

0.8059 grm.

0.8062 grm.

The copper sulphate, which was left unaltered in the filtrate, was then determined as oxide; the amounts of oxide were found to be—

0.5325 grm.

0.3454 grm.

which are equivalent to—

1.6783 grm. and 1.0886 grm.

of copper sulphate. We therefore get, adding together these separately determined quantities,—

0.8059

0.8062

1.6783

1.0886

2.4842 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

1.8948 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$,

which agree very well with the quantities of copper sulphate which were taken,

2.4840 grms. and 1.8945 grms.,

at the beginning of the investigation.

Here, then, no other formula than CuS will represent the compound formed under these conditions, and so the statement that cupric sulphide is unknown requires modifying.

As regards the alleged Cu_4S_3 , of which more anon, may it not be due to a want of saturating the solution with hydrogen sulphide? Just as in the case of mercury and lead, different compounds of the type MS, MCl_2 are formed with colour changes, according to the amount of hydrogen sulphide passed in, but which ultimately go to MS completely,

BORON BRONZE.

By H. N. WARREN, Research Analyst.

THIS alloy—or, more correctly speaking, aluminium boron bronze—is brought about by the introduction of aluminium containing boron, not as aluminium boride, but existing as graphite does in cast-iron. Commercially this part of the process is accomplished by heating, in a specially-constructed oxyhydrogen furnace, an admixture of fluor-spar and vitrified boric anhydride, until the dense fumes of boron fluoride commence to appear. At this stage ingots of aluminium are introduced into the liquid mass; reduction at once takes place, with the formation of free boron, which dissolves in the aluminium, rendering it crystalline and somewhat brittle. When this so-prepared aluminium is alloyed with copper to the extent of from 5 to 10 per cent, a bronze is obtained, denser and more durable than ordinary aluminium bronze, and free from brittleness; but the most important property of the alloy is the readiness with which it melts and casts, whereas in the manufacture of aluminium bronze one of the greatest

difficulties is to ensure an uniform mixture. Often a very difficultly fusible alloy of copper and aluminium is formed upon the surface of the already liquid portion, and accompanied by superficial oxidation, thus obstinately refusing to alloy with the remainder. But in the case of the boron compound no such difficulties are met with, the alloy melting perfectly and at lower temperature than when employing pure aluminium. Boron, in fact, seems to have been but little studied, but it is evidently not so serious an enemy to cope with as its halogen silicon, which, when present in minute percentages only, determines the total ruin of the bronze with which it alloys; in other words, it stands almost entirely opposite to other elements, entering into the formation and forming compounds with the most refractory minerals with the greatest ease; for instance, borides of iron, manganese, nickel, cobalt, &c., may be readily formed by the reduction of their accompanying borates in the presence of carbon, whilst those of silver, gold, &c., can only be formed by the introduction of elementary boron into the fused mass; borides of the alkali metals, and even barium and calcium, have been obtained, but boride of mercury still remains unknown,

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CHEMICAL RESEARCHES AND SPECTROSCOPIC STUDIES OF VARIOUS ELEMENTS.

By JEAN SERVAIS STAS.

(Concluded from p. 250).

WHEN working in a dark room I obtained the following positions of the line in the flame spectrum; D being 50°00:—

		Difference from the mean.
Metal	65°40	-0°10
	65°25	-0°25
	65°60	+0°10
Chloride	65°60	+0°10
	65°45	-0°05
	65°65	+0°15
Sulphate	65°30	-0°20
	65°45	-0°05
	65°60	+0°10
Nitrate	65°55	+0°05
	65°70	+0°20
	65°40	-0°10
Mean	65°50	

The mean, then, is 65°50, with a mean error of ± 0.125 equal to that found when measuring Fraunhofer's lines. I may say that the measurement of the centre of a brilliant fixed line appears to me to be easier, and susceptible of a greater degree of accuracy, than that of one of Fraunhofer's lines.

To measure the position of the line in the electric spectrum of thallium, I substituted for the fixed blowpipe, successively, a *short* spark from a coil without a condenser, passing between thick platinum wires terminating in pure iridium balls, well coated either with metallic thallium or its chloride, and a *short* electric arc, passing between small cones of pure carbon, also well covered with thallium or its chloride. I put the insulated carrier on the right-hand support in front of the collimator, at a suitable height. I arranged the platinum wires, ending in covered balls or carbon cones, horizontally. By working the endless screw of the right-hand support I brought the centre of the interval between the balls or cones into the axis of the collimator, and I marked this support and the table carrying the spectroscope, so that I might always

be able to bring the centre of the interval between the poles to the same position.

Having made the 50th micrometer division coincide with Fraunhofer's D line, the current being previously made by contact of the cones, I brought the cross wires to the centre of the thallium line. Whilst letting the sparks continue, I worked the endless screw of the right-hand support so as to *displace* the balls and cone, in such a manner as to make the thallium line disappear. Then, by means of the endless screw, the centre of the space between the balls and cones was brought to its former position; this was most quickly done by adjusting the support to the marks. I *estimated* the position of the cross wires, which were unmoved, compared with the centre of the re-formed thallium line. Between each displacement and replacement I ascertained, by passing a ray of sunlight, that the 50th scale division coincided properly with Fraunhofer's D line. In a comparatively short time I was able to make the thallium line appear and disappear *five times*, and thus measure the change in the position of the centre of this line.

I have, besides, checked the observations made by this method of ascertaining the displacement undergone by the centre of the line, by repeating the measurement from the moment the line appeared until it disappeared, owing to the gradual movement back and forward of the space between the balls and cones coated with thallium or one of its compounds.

I found thus that, for a distance of 5 or 6 m.m. between the poles, the displacement was insensible for two-thirds of this distance; it was less than the personal error in measuring the position occupied, in comparison with the centre of the line, by the cross-wires which were projected on it in black.

The following are the results of the very fatiguing observations I made in a dark room:—

A. In the centre of the spark, from 3 to 5 m.m. long.

		Difference from the mean.
1st. With metallic thallium ..	65°60	+0°10
	65°45	-0°05
	65°55	+0°05
	65°40	-0°10
	65°55	+0°05
2nd. With chloride of thallium .	65°45	-0°05
	65°60	+0°10
	65°50	+0°00
	65°40	-0°10
	65°65	+0°15

B. In the centre of an electric arc, from 3 to 4 m. m. long.

		Difference from the mean.
1st. With metallic thallium ..	65°35	-0°15
	65°55	+0°05
	65°60	+0°10
	65°45	-0°05
	65°55	+0°05
2nd. With chloride of thallium .	65°70	+0°20
	65°45	-0°05
	65°40	-0°10
	65°55	+0°05
	65°50	+0°00
Mean	65°51	

The mean of the measurements was therefore 65°51, with a mean error of ± 0.085 . The mean of the measurements of the position of the thallium line in the flame spectrum being 65°50, with a mean error of ± 0.125 , I therefore conclude that the position of the thallium lines in the electric and flame spectra are identical.

When using the large Hilger spectroscope with its six Iceland spar prisms, and taking the *solar spectrum* as a basis of comparison, I found, with absolute certainty, that the positions of the thallium line seen successively in an

oxyhydrogen *blowpipe* and in an electric arc charged with thallium were identical.

Since these experiments were carried out, and this chapter written, I have had occasion to submit the above observations to a fresh check. Messrs. Liveing and Dewar having kindly put at my disposal the new direct-vision spectroscopic designed by them, I was pleased to be able to use this excellent instrument to verify the respective positions of the flame and the electric thallium lines; I found *the position of the two lines to be identical.*

Thallium thus resembles carbon and potassium, for their flame and electric lines respectively occupy the same position in the spectrum.

In collaboration with M. Depaire I revised the above-described work, and especially the observations on the singleness of the line and the position of the flame and electric thallium spectra, and on the masking of a weak sodium spectrum, in other words, on the non-visibility of the D line under the influence of thallium rays.

We made these observations by using, on the one hand, the metallic thallium and its trioxide, chloride, bromide, nitrate, and sulphate, used during the above-described researches, and, on the other hand, by using some sulphate prepared by M. Depaire.

To carry out this check, we used in succession a single glass prism and a double flint-glass prism spectroscopic by M. Duboscq; a double quartz prism instrument by Hilger; an instrument by Hilger fitted with a Chapmann grating; and lastly, the direct-vision spectroscopic by Messrs. Liveing and Dewar, the dispersive power of which was equal to the Duboscq spectroscopic with its five 60° prisms. Whatever thallium compound we used, whether we examined the flame spectrum in air or the electric spectrum in hydrogen, the results were exactly the same as those described above.

We found that the flame and electric spectra of thallium consisted of a single intense green line, just as described by Bunsen in his "Nouvelles Recherches," and we found the position of this single line in the two spectra to be the same. When using a spectroscopic furnished with a grating instead of prisms, we were unable to split up or cause a double reversal of the thallium line.

We checked these results in an electric arc 2½ c.m. long by about 8 m.m. diam., passing between pure carbon electrodes. This check enabled us to make the following observations:—

A. As regards the appearance of the electric arc charged with thallium:—

On dropping into the crater of the arc, by means of a pure carbon needle, some thallium or one of its compounds, such as chloride or sulphate, but preferably a drop of pure metal, it was noticed:—1st, that the deep blue colour of the arc instantly became *pale blue*; 2nd, that the part of the envelope of the arc which was red, became *sparkling white*; 3rd, that the pink outer zone of the arc was coloured *intense green*.

By continuing to introduce metallic thallium into the arc until the air was filled with thallium vapour, which was very dangerous to breathe, we found the preceding observations to be perfectly exact.

At the temperature of the arc, vapour of thallium appears then to be pale or sky blue. The colours of the first and second zone varied with their temperatures, which are below that of the arc.

B. As regards the spectrum of the carbonate charged with thallium:—

At the moment of introducing thallium into the arc, it was noticed that the luminosity of the carbon lines, which varied moreover with the distance between the arc and the collimator, was greatly increased, but that this luminosity was immeasurably inferior to that of the very bright and intense green thallium line interposed between the comparatively pale green carbon lines. The position of the interposed thallium line was exactly the same as that it occupied in the flame and electric thallium spectra. All our efforts to verify the appearance of other lines, on

either side of the green thallium line, properly so called, were in vain. When using the Hilger spectroscopic with a Chapmann grating, we could not split up the thallium line or effect the double reversal, a thing which is so easily done with the D line in the electric sodium arc.

Observation of the flame or electric thallium spectrum, *by the eye*, shows only the single green line. This metal is not susceptible of being dissociated into any other bodies by the forces we have actually at our disposal. It is a true element, as are the other bodies which have been the subject of my investigations.

A REVISION OF THE ATOMIC WEIGHT OF ZINC.*

FIRST PAPER: THE ANALYSIS OF ZINCIC BROMIDE.

By THEODORE WILLIAM RICHARDS
and
ELLIOT FOLGER ROGERS.

(Concluded from p. 251).

Method of Analysis.—Perhaps the best method of explaining the method of analysis is to give a detailed description of a single determination; and for this purpose Analyses 15 and 19, in which both silver and argentic bromide were weighed, will best serve.

The very pure sublimed zincic bromide was pressed into a platinum boat; and the boat was placed in a tube of hard glass, which had been ground into another tube designed to contain a weighing bottle. The apparatus consisted essentially of a combination of the two pieces of apparatus already shown (Figs. 1 and 2); it was devised for a research upon the atomic weight of magnesium now being carried on by Messrs. Richards and Parker, and it will be described in full when that investigation is published. With the help of this apparatus it was possible to heat the zincic bromide to any temperature below its boiling-point in an atmosphere of pure dry air, pure dry carbon dioxide, or pure dry carbon dioxide charged with hydrobromic acid; and these gases could be changed at will merely by the opening and closing of stopcocks. When the heating had been continued for the desired length of time, it was possible to push the boat into the weighing-bottle and to stopper the weighing-bottle very tightly in a perfectly dry atmosphere, without the least chance of the absorption of moisture from the outside air. All the apparatus which could possibly come into contact with bromine or hydrobromic acid was made of glass, with ground-glass joints and glass gridirons for convenient re-filling.

The zincic bromide was heated very gradually at first in an atmosphere of carbon dioxide which had been dried by passing over sulphuric acid, fused zincic bromide, and phosphorus pentoxide. If heated very gradually in this way, zincic bromide may be almost wholly dehydrated without loss of bromine; but a basic bromide is certain to form if the heating is rapid. When all of the apparent water had been expelled from the substance and its containing tube, dry hydric bromide was added to the carbonic dioxide, and the temperature was gradually raised to the fusing-point of zincic bromide. The bromide was kept at a temperature just above its melting point for about an hour; during this time perhaps a tenth of the substance sublimed in the exit end of the "combustion" tube—rendering the drying tube, which had been ground on to protect the exit, unnecessary. It was assumed that at the end of an hour the fused zincic bromide must be as free from water and from basic salt as it was possible to obtain it; accordingly, the temperature was allowed to fall to about 200°, and the current of dry hydrobromic

* Contributions from the Chemical Laboratory of Harvard College. From the *Proceedings of the American Academy*. Presented April 10, 1895.

acid was stopped. Soon air—dried by means of sulphuric acid, fused potash, and phosphorus pentoxide—was substituted for the carbon dioxide, the temperature being allowed to fall to about 150° to avoid any possible decomposition of the zincic bromide; and this current of air was continued for several hours until long after every trace of hydrobromic and carbonic acid had been swept away. In order to “make assurance doubly sure,” the whole length of the tube, weighing-bottle and all, was heated to 100° or more several times, in order to prevent any possible occlusion of acid. When all was in readiness, the warm boat was pushed by means of a long glass rod into the weighing-bottle, and the bottle was stoppered with the help of the same rod. The apparatus was then pulled to pieces, the closed bottle was transferred at once to a tight desiccator, and after a suitable rest of several hours, it was weighed with all possible care. The various weighings are tabulated below. (For detailed method see *Proc. Amer. Acad.*, xxviii., 5).

	Common weights, right-hand pan.	Tare : Standard weights, left-hand pan by substitu- tion.	Standard weights corrected.
	Grms.	Grms.	Grms.
Weight of boat beforehand..	7.7693	7.76937	7.76932
“ “ + bottle ..	19.9757	0.00372	0.00372
The same + ZnBr ₂ after seven hours' cooling ..	25.2389	5.26754	5.26747
After two more hours ..	25.2389	5.26754	5.26747
After two hours' standing in balance	—	5.26757	5.26750
Weight of boat after expt. . .	7.7693	7.76938	7.76933
Boat + bottle afterward ..	19.9757	0.00375	0.00375
Gain of boat	—	—	0.00001
“ “ + bottle	—	—	0.00003
Average tare of boat + bottle + ZnBr ₂	—	—	5.26748
Average tare of boat + bottle	—	—	0.00373
Weight of ZnBr ₂ in air ..	—	—	5.26375
Correction to vacuum, 20° and 762 m.m.	—	—	0.00074
Weight of ZnBr ₂ in vacuum	—	—	5.26449

Before having been treated with water, the bottle and boat were allowed to stand for twenty hours in somewhat moist air. During that time they gained only two-tenths of a m.grm., showing that the diffusion of moisture through the stopper was very slow. In order to prove the efficiency of the drying and fusing apparatus, the bottle with its contents were returned to it, and the stopper was removed by means of a wire, while a current of dry air was allowed to pass through the whole apparatus. This current was continued for half an hour, the boat and bottle being warmed to about 120°. After suitable cooling, the substance was found to have lost one-tenth of a m.grm., being one-tenth heavier than it was in the first place. These weights were not included above, in order to avoid complications; they do not belong necessarily to the analysis, but merely serve to show that the apparatus was wholly sufficient for its purpose.

The boat and its contents were conveyed with great care to a large Bohemian beaker, and the weighing-bottle was rinsed out many times with the purest water. When the zincic bromide had wholly dissolved, the perfectly clear solution was transferred through a large funnel to the glass-stoppered Erlenmeyer flask intended to serve for the precipitation. The boat was easily washed by allowing it to rest in the funnel; and, of course, beaker and all were rinsed with the most scrupulous care. The total

volume of the thus diluted zincic bromide amounted to about 250 c.c.

The silver to be used for the precipitation weighed 5.04328 grms. in the air, or 5.04313 grms. in vacuum. It was dissolved in 10 c.c. of nitric acid, diluted with water, in a large flask provided with a bulb tube, and the absolutely clear solution was freed from lower oxides of nitrogen by standing upon the steam-bath. The contents of the bulbs, usually containing only a few hundredths of a m.grm. of silver, were washed back into the flask, and the whole was diluted to about half a litre.

The addition of the argentic nitrate to the zincic bromide took place in the dark room (see previous papers upon Barium and Strontium), and great pains were taken to prevent exposure of the materials to anything but non-actinic light from this time until the final weighing of the argentic bromide. Of course, every trace of silver was washed into the flask containing the zincic bromide. After the whole had been very thoroughly shaken and allowed to stand for several days, 0.21 c.c. of hydrobromic acid (1 c.c. was equivalent to a m.grm. of silver) failed to produce an evident precipitate, even when the solution was lighted by a brilliant condensed beam of yellow light. On the other hand, 0.60 c.c. of an equivalent solution of silver produced an evident cloudiness; 0.40 c.c. more also produced a cloud. Still, 0.20 c.c. gave a very faint indication of opalescence, after a long time; and, finally, 0.21 gave no trace. On titrating back with hydrobromic acid, it was necessary to add 1.21 c.c. more before the point was reached where an extra 0.20 produced no precipitate. The total amount of silver solution added was then 1.41 c.c., or 0.21 to precipitate the first amount of hydrobromic acid added, 0.21 to show that all the bromine was precipitated, and 0.99 to correspond to the true amount of silver to be added in order to attain the end-point; while the total amount of hydrobromic acid added to reach the end-point in the other direction was 1.42 c.c., an amount which must be subtracted from the amount of silver added. Hence, since the true amount of silver corresponding to the zincic bromide is the mean between the amounts found by titrating in opposite directions (*Proc. Amer. Acad.*, xxviii., 24; xxix., 74; xxx., 384), we obtain it as follows:—

Amount of Silver Required.		Grms. in vacuum.
Titrating with ar- gentic nitrate ..	5.04313 + 0.00099	= 5.04412
Titrating with hy- drobromic acid .	5.04313 + 0.00141 - 0.00142	= 5.04312
Average: silver required..		5.04362

Since it is hardly probable that the end-point may be obtained by this method more nearly than the tenth of a m.grm., the last figure is omitted below.

If, as is probable, the action of silver and hydrobromic acid in preventing the solution of silver bromide resembles the action of silver and hydrochloric in precipitating solutions of silver chloride (Stas), the difference between the end-points 1.00 m.grm. of silver) corresponds to six times the amount of argentic bromide dissolved; that is, this amount must be about 1.74 or 0.29 m.grm. in 0.85 litre of a solution containing 2 or 3 c.c. of nitric acid and about 5 grms. of zincic nitrate.

In order to precipitate all the bromine, 4 m.grms. more of argentic nitrate were added to the solution, and the whole was very vigorously shaken. After a day or two, the mixture was filtered through a weighed Gooch crucible, and the precipitate was shaken and allowed to stand with many successive portions of water containing 5 m.grms. of argentic nitrate to the litre. It was finally transferred quantitatively to the crucible, washed with pure water to remove the traces of argentic nitrate, and dried at 160° in a porcelain drying oven in a stream of air purified by passing over sulphuric acid and potash. The

2 litres of filtrate were allowed to stand until the shreds of asbestos had settled; and these were collected upon three thicknesses of the best filter paper, ignited, and weighed. The main body of the precipitate was transferred to a porcelain crucible, weighed, fused in a porcelain oven, and weighed again. Below are the data:—

	Common weights.	Standard weights by substitution.	Standard weights corrected.
	Grms.	Grms.	Grms.
Gooch crucible alone	18.4812	0.22840	0.22840
„ „ + AgBr	27.2633	9.01052	9.01050
Argentio bromide in air	—	—	8.78210
Correction to vacuum	—	—	0.00039
Chief mass of argentio bromide in vacuum	—	—	8.78249
Porcelain crucible + AgBr	25.6757	8.37781	
The same after fusion	25.6755	8.37760	
Loss on fusion	—	0.00021	0.00021
Crucible + ash + asbestos	15.2857	0.05284	
Crucible	15.2853	0.05226	
Ash + asbestos	—	0.00058	
Ash of three filters	—	0.00012	
Asbestos	—	0.00046	0.00046
Total weight of AgBr	—	—	8.78274
Subtract amount corresponding to $1.42 + 0.20 = 1.62$ c.c. HBr solution	—	—	0.00282
Argentio bromide corresponding to zinc bromide	—	—	8.77992

Thus, 5.26449 grms. of zinc bromide correspond to 5.0436 grms. of silver and 8.77992 grms. of argentio bromide. If bromine and silver are taken as 79.955 and 107.93 as usual, the atomic weights of zinc computed from these ratios are identical—65.404. Since this is the case, of course the per cent of silver found in argentio bromide $\frac{5.0436}{8.77992} \times 100$ is identical with that obtained by Stas, or 57.445.

In no one of the other determinations were both silver and argentio bromide determined, hence the others were simpler in execution, although essentially the same in principle. The end-point in Analysis 17 was probably not determined more nearly than two-tenths of a m.grm., while that in Analysis 19 was determined by the nephelometer (*Proc. Amer. Acad.*, xxx., 385) much more accurately even than in the detailed determination. Indeed, this value was so accurate that the hundredths of a m.grm. may have some significance, although the weights taken were so large. The data of all these final determinations are given below:—

FINAL DETERMINATIONS.

The Ratio of Zinc Bromide to Silver.

No. of analysis.	Weight of zinc bromide.	Weight of silver.	Ratio. $\frac{\text{ZnBr}_2}{2\text{Ag}}$.	Atomic weight of zinc.
	Grms.	Grms.		
14.	6.23833	5.9766	104.379	65.403
15.	5.26449	5.0436	104.380	65.404
16.	9.36283	8.9702	104.377	65.398
Average			104.379	65.402

In this determination the only serious possibility of error is that the zinc bromide may have contained a lingering trace of water in spite of the elaborate precautions adopted to secure its absence. It is hoped that before long a determination of the zinc, as well as of the

The Ratio of Zinc Bromide to Argentio Bromide.

No. of analysis.	Weight of zinc bromide.	Weight of argentio bromide.	Ratio. $\frac{\text{ZnBr}_2}{2\text{AgBr}}$.	Atomic weight of zinc.
	Grms.	Grms.		
17.	2.65847	4.43358	0.599622	65.410
18.	2.30939	3.85149	0.599606	65.404
19.	5.26449	8.77992	0.599606	65.404
Average			0.599611	65.406
From the first ratio, if O = 16				Zn = 65.402
From the second ratio, if O = 16				Zn = 65.406
Average, if O = 16				Zn = 65.404
If O = 15.96				Zn = 65.240
If O = 15.88				Zn = 64.912

bromine in zinc bromide, may be made in this laboratory, furnishing evidence upon this point. However, since the figure given above agrees closely with the probable corrected result of Morse and Burton's investigation, as well as with the somewhat incomplete determinations of Baubigny, and Gladstone and Hibbert, the value 65.40 may be safely adopted for the present as the most probable value of the atomic weight of zinc.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 21st, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

MR. THOMAS B. CASE was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. John Henry Garrett, Cheltenham; Leon Felix Goldstand, 12, Quai Anglais, St. Petersburg; Alfred Griffiths Greenway, Llandrindod Wells, N. Wales; Ernest George Hill, Muir College, Allahabad; Joshua Arthur Hughes, Abercarn, Monmouthshire; Herbert E. Law, 1526, Vallego Street, San Francisco; Asutosh Mitra, Kashmir; Samuel Thomas Skelton, 13, Derby Street, Ramsbottom, near Manchester.

Mr. J. Morrow Campbell is reinstated as a Fellow.

The following papers were read:—

69. "The Diphenylbenzenes. I. Metadiphenylbenzene." By FREDERICK D. CHATTAWAY, M.A., and R. C. T. EVANS.

Three isomeric diphenylbenzenes, $\text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_2$ are possible, but up to the present only two compounds having this formula are known,—paradiphenylbenzene, and the so-called isodiphenylbenzene. The constitution of the former is established, as it has been obtained from paradibromobenzene, and yields on oxidation paradiphenylcarboxylic acid and terephthalic acid; the constitution of the latter is still doubtful.

The authors have undertaken the synthesis of ortho- and metadiphenylbenzene, and this paper contains an account of the first part of the investigation.

When benzene vapour is led through a red-hot tube, a mixture of hydrocarbons is obtained, and from the portion distilling at temperatures near 400° paradiphenylbenzene and the so-called isodiphenylbenzene have been isolated. This latter, on oxidation, yields chiefly a mixture of benzoic, paradiphenylcarboxylic, and terephthalic acids. No conclusion as to its constitution can be drawn from this, although the fact that its monobromo-derivative yields, on oxidation, an acid which, on reduction, yields diphenyl-

metacarboxylic acid, shows that the phenyl groups probably occupy meta positions.

Having obtained metadichlorobenzene in large amount, the authors have synthesised from this metadiphenylbenzene, which proves to be identical with the isodiphenylbenzene obtained from benzene. The hydrocarbon was obtained by the action of melted sodium on a mixture of metadichlorobenzene and chlorobenzene dissolved in boiling xylene. It is easily separated from the other products of the action by fractional distillation.

Metadichlorobenzene appears to have very slight action on benzene in the presence of anhydrous aluminium chloride, and the hydrocarbon cannot be prepared in this way.

Metadiphenylbenzene is a colourless substance, easily dissolved by ordinary solvents, and crystallising in star-shaped groups of fine needles. It melts at 84° , and boils at about 369° under a pressure of 766 m.m. Its composition and molecular weight, determined by Raoult's method, using benzene as a solvent, agree very closely with those required by the formula $C_6H_3(C_6H_5)_2$.

70. "Derivatives of Camphoric Acid." By F. STANLEY KIPPING, Ph.D., D.Sc.

The paper contains an account of numerous derivatives of camphoric acid which have been prepared from π -bromocamphoric acid, and some of which have been briefly described in previous notes (*Proc.*, 1895, cxlviii., 33; cli., 88; clvii., 210); the formation, properties, and relation to one another of all these substances are explained on the basis of Brecht's formula for camphoric acid.

The lactonic monocarboxylic acid, $C_{10}H_{14}O_4$ (m. p. 165°), which is produced when an aqueous solution of sodium π -bromocamphorate is boiled, is derived from trans- π -hydroxycamphoric acid, $C_{10}H_{16}O_5$ (m. p. 131°), whereas the more stable isomeride (m. p. 226°) is the lactone of a cis- π -hydroxycamphoric acid, which seems not to exist except in the form of a salt. These lactonic acids are named trans- π -camphanic acid and cis- π -camphanic acid respectively, in order to recall the fact that they are isomeric with, and closely related to the w -camphanic acid, which is derived from w -bromocamphoric acid (*Trans.*, 1896, lxix., 61).

Trans- π -camphanic anhydride, $C_{20}H_{26}O_7$, crystallises in prisms of indefinite melting-point; the isomeric anhydride of the cis-acid crystallises in plates or prisms, melting at $164-165^{\circ}$.

Trans- π -camphanamide, $C_9H_{13}O_2 \cdot CO \cdot NH_2$, is obtained when methylic π -bromocamphorate (m. p. $114-115^{\circ}$) is treated with aqueous ammonia; it crystallises from aqueous ammonia in transparent octahedra, and melts at $114-115^{\circ}$.

Methylic cis- π -camphanate crystallises in prisms melting at 75° . w -Hydroxy-cis- π -camphanic acid, $C_{10}H_{14}O_5$, prepared by oxidising cis- π -camphanic acid with potassium permanganate, separates from water in transparent, hydrated prisms, and melts at $264-265^{\circ}$.

w -acetoxy-cis- π -camphanic acid, $C_{10}H_{13}O_5(OAc)$, is formed when the hydroxy-acid is heated with acetyl chloride; it crystallises well, and melts at $123-124^{\circ}$.

π -acetoxycamphoric anhydride, $C_{12}H_{16}O_5$, prepared by treating trans- π -hydroxycamphoric acid with acetyl chloride, crystallises in monosymmetric plates, and melts at $86-87^{\circ}$ (at $89-90^{\circ}$ on re-heating).

When trans- π -camphanic acid or π -hydroxycamphoric acid is oxidised with nitric acid, it is converted quantitatively into a tricarboxylic acid of the composition $C_{10}H_{14}O_6$ (m. p. 196°), which is named trans-camphotricarboxylic acid; this substance crystallises from water in massive orthorhombic pyramids, and is extremely stable towards ordinary oxidising agents; its formation from π -hydroxycamphoric acid shows that the latter substance contains the group $-CH_2OH$, and consequently the π -substituent in all these π -derivatives has displaced hydrogen from a methyl group.

Trans-camphotricarboxylic anhydride, $C_{10}H_{12}O_5$, forms monosymmetric crystals and melts at $253-254^{\circ}$.

Two isomeric lactones are formed when trans-camphotricarboxylic acid is treated with bromine and amorphous phosphorus at 100° and the product then warmed with water; these compounds have the composition $C_{10}H_{12}O_6$, and are both derived from a πw -dihydroxycamphotricarboxylic acid of the composition $C_{10}H_{14}O_7$. The one (β -lactone) crystallises in six-sided plates, and melts at 220° ; the other (γ -lactone) crystallises in flattened needles of indefinite melting-point, and is formed from the isomeride by heating the latter with alkalis and then acidifying.

Cis-camphotricarboxylic acid, $C_{10}H_{14}O_6$, is obtained as a salt when the trans-acid is fused with potash; it crystallises in massive transparent prisms, and has no definite melting-point, owing to the ease with which it is converted into its anhydride.

Cis-camphotricarboxylic anhydride, $C_{10}H_{12}O_5$, is formed when the trans-acid is heated alone or with concentrated sulphuric acid; it crystallises from benzene in prisms which effloresce in the air and melt at 220° .

71. "On some Substances which exhibit Rotatory Power both in the Liquid and Crystalline States." By WILLIAM JACKSON POPE.

Although a very large number of organic substances are known which in the liquid or amorphous condition rotate the plane of polarisation of a polarised ray passing through them, very few crystalline substances are known which exhibit this same property; a still smaller number of substances are known which exhibit circular polarisation both in the amorphous and crystalline condition.

Substances which exhibit circular polarisation when amorphous very frequently crystallise in those crystalline sub-systems in which enantiomorphism is possible, losing during the process of crystallising the power of circularly polarising light; during crystallisation, the latter property is in some way compensated for by the crystalline structure, which has neither planes nor a centre of symmetry. The exact connection between the crystalline form and optical activity of circularly polarising substances is as yet by no means settled, and any remarkable cases of crystallisation of such active substances consequently possess great importance.

Two substances only, viz., matico camphor and rubidium tartrate, are known which possess the power of circularly polarising light in both the amorphous and crystalline states. The author now describes a third case, that of cis- π -camphanic acid, which crystallises in the pyramidal hexagonal system; when viewed between crossed nicols, the hexagonal optic axial picture is seen to be of the peculiar appearance characteristic of circularly polarising hexagonal crystals. The crystals are strongly pyroelectric, and are laevorotatory, the specific rotation being thus of the same sign as that of the amorphous or dissolved substance.

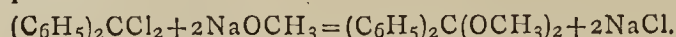
Although so few cases of the occurrence of true circular polarisation in both amorphous and crystalline states are known, a large number of optically active substances are known, the crystals of which do, in parts, exhibit circular polarisation. The latter phenomenon is, however, due to more or less complicated twinning; it is not a result of the actual molecular structure of the crystal, but of the superposition of thin laminae of the crystal. These cases should consequently not be considered as true examples of the occurrence of circular polarisation in the two states. Circular polarisation caused by the piling up of thin plates of biaxial crystals at definite angles to each other has been demonstrated by Reusch, who arranged cleavage flakes of mica one on the other in a definite sense, the optic axial planes of any piece being at 60° to those of the two plates in contact with it; the resulting pile is uniaxial and circularly polarising. A very beautiful example of this kind of circular polarisation is found in the hydrated crystals of the optically active trans-camphotricarboxylic acid (see preceding paper); this substance crystallises in

six-sided plates which simulate hexagonal symmetry, but are really composed of six sectors of an orthorhombic crystal. At the edges of the plates, where no overlapping of the sectors occurs, the biaxial interference figure of the orthorhombic crystal can be seen, whilst in the centre of the plate, where the sectors meet and overlap, the optic axial plane of each sector being at 60° with those of its two neighbours, a uniaxial interference figure is seen and circular polarisation is observed.

The crystals of this substance thus afford a very striking imitation of Reusch's circularly polarising piles of mica plates.

72. "*Dimethoxydiphenylmethane and some of its Homologues.*" By JOHN E. MACKENZIE, Ph.D., B.Sc.

This compound was prepared by the action of sodium methylate on benzophenone chloride, according to the equation—



The chloride was added to the alcoholic solution of the sodium methylate, and after reaction had taken place, the whole was heated in a water-bath for two hours. The substance was obtained pure by re-crystallisation from alcohol, the yield being 81 per cent of the calculated. The crystals are perfectly colourless and odourless, melt at $106.5-107^\circ$, and boil at $288-290^\circ$ without decomposition. They are easily soluble in ether, hot methyl and ethyl alcohols, and benzene, but less so in the cold, insoluble in water. The substance is volatile with steam. It is unaffected by alkalis, but is decomposed by acids, forming benzophenone. In a desiccator over sulphuric acid it loses ether.

Diethoxydiphenylmethane, $(C_6H_5)_2C(OC_2H_5)_2$, is prepared similarly. Yield, 85 per cent of the calculated. The colourless crystals melt at $51.5-52.2^\circ$. The solubility and general behaviour are similar to the methoxy-compound.

Dibenzoxydiphenylmethane, $(C_6H_5)_2C(OC_7H_7)_2$, is prepared similarly, except that the mixture of chloride and the sodium derivative of the alcohol is heated to $205-210^\circ$. The crystals melt at $104-105^\circ$, and decompose when distilled. They deliquesce on exposure to air. They are easily dissolved by the ordinary solvents when hot, with difficulty when cold.

NOTICES OF BOOKS.

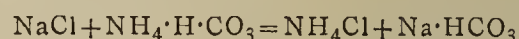
A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali, with the Collateral Branches. By GEORGE LUNGE, Ph.D., Professor of Technical Chemistry at the Federal Polytechnic School, Zurich; (formerly Manager of the Tyne Alkali Works, South Shields). Second Edition, Revised and Enlarged. Vol. III. 8vo., pp. 840. London: Gurney and Jackson (Van Voorst's Successors). 1896.

As the author informs us in his Preface, and as the reader indeed would have no difficulty in discovering for himself, we have here to do not with a new edition in the ordinary sense of the words, but with a new book for which the old edition serves as a basis. The chapters on Ammonia-soda and on the Deacon Process have been entirely re-written, and the section on Electrolysis now appears for the first time.

We read here, what our own experience in several departments of technical chemistry corroborates, that "very few of what practical men take to be important secrets are not accessible in print in one shape or other, or are not known just as well to other practical men." The author has often found that information received as "strictly confidential" was to be obtained in full in the form of patent specifications.

The history here given of the ammonia-soda process is

extremely interesting. The real inventors were undoubtedly H. G. Dyar and J. Hamming, both of London. On June 30th, 1838, they took out an English patent, in which the reaction—



is distinctly set forth. A variety of experiments were made, and one establishment—that of Barker, near Leeds—put alkali on the market for several years. Commercially speaking, the process was a failure, chiefly on account of the loss of ammonia. Solvay's ultimate success depended not on any improvement in principle, but merely on superior mechanical arrangements by which this waste was prevented. Solvay seems to have been under the impression that he had been the first to discover the reaction of the ammonia-soda process. He had, according to Dr. Lunge, "an almost fanatical belief in the enormous value of the process," and was ignorant of the numerous and costly failures already made: had he been aware of the previous career of the invention, he would scarcely have staked his own means and those of his friends on the result. It is here remarked that Solvay's procedures do not present the only solution of the problem. "There exist a number of ammonia-soda works, carried on successfully and profitably, with apparatus differing totally from Solvay's, and preferred by their owners to his, although his patents have now lapsed."

A tabular view here given sums up the respective cost per ton of 58 per cent ammonia-ash and 55 per cent Leblanc ash as £2 18s. 9d. and £3 1s. 11d. This is a very decided advantage for the ammonia process. The repairs in the latter process are very heavy, as ammonia acts upon all iron appliances, upon caoutchouc washers, &c.

In England the consumption of salt for the ammonia process was in 1884 only 80,759 tons, but in 1893 it had risen to 349,609 tons. The great disadvantage of the success of the ammonia process is that it cuts off the supply of cheap hydrochloric acid. Any process which requires such acid is in great peril or has to be abandoned. Instance three procedures for the production of crude aluminium hydrochlorate to be used in the purification of sewage.

Among the almost numberless methods proposed of obtaining alkali, mention is made here (Eng. Pat. 11,008, 1884) of a mixture of nitrate and coal-dust compressed and heated to combustion. The mass is lixiviated, and the solution is brought to crystallisation or converted into bicarbonate by means of the CO_2 obtained by burning the carbon monoxide formed in the first reaction. Our author drily remarks that this invention is probably the outcome of popular evening classes on chemistry, a certain lady having taken out no fewer than three patents in this connection.

The third book treats of the chlorine industry. The great turning-point in the history of the art was Tennant's patent for the absorption of chlorine in dry hydrate of lime. As regards the physiological action of chlorine, we find the statement that persons accustomed to chlorine can tolerate 1 vol. in 10,000 of air. Weigelt finds that 0.005 grm. free chloride per litre kills trout in a few minutes. The use of magnesium chloride as a source of free chlorine has given rise to great hopes and numberless experiments, but hitherto without any marked success. For a long time the exclusive process for obtaining chlorine was the action of hydrochloric acid upon manganese ore or Weldon mud.

All the proposals for recovering the manganese have resulted in failure except those of Dunlop and of Weldon. Of these methods the former has now been practically abandoned.

In the Deacon process for the production of chlorine, manganese is not economised as in the Weldon process, but is entirely superseded.

On page 378 we find a most interesting note, on the uncertainty of all predictions founded on thermo-chemical

data, for which, however, we must refer to the work itself.

In spite of the great advantages of the Deacon process the greatest part of the bleaching-powder made in Britain was in 1895 still produced by the Weldon process.

In Chap. XX., discussing the manufacture of bleaching-powder, the quality of the lime employed is fully insisted on. "Fat lime," such as that of Buxton, is much preferable to poor limes which on slaking yield a gritty powder.

The author protests against the low chambers of 5 feet or lower, as both inhuman to the workman and unfavourable to good uniform working. Cases of the explosive decomposition of bleaching-powder have occurred chiefly when warm bleach has been packed in hot weather.

The fourth book of the work enters very thoroughly into the preparation of alkalis, chlorine, and chlorates by electrolysis.

The author quotes, from the *Chem. Zeitung*, Quincke's discourse on the utilisation of energy when transformed into the electric current. The loss when the steam-engine and the dynamo are used is most serious. Dr. Lunge queries Quincke's assertion that hitherto this is the only source of electricity available in practice. At present he holds that the cheapest source of electricity is water-power, with the dynamo directly coupled on to the turbine. Hence in industry the future belongs to those countries which are rich in water-power. Hurter concludes that "for the production of articles at low price, electrolysis as a manufacturing operation is impracticable." This view was expressed in 1888, but since that time Dr. Hurter has apparently modified his opinions.

In the electrolytic production of soda and chlorine "nearly everything depends upon employing good anodes and diaphragms," and here accordingly is good scope for the inventor.

On the electrolytic methods for the purification of sewage and similar foul waters (Hermite and others), no very decided conclusion has been reached. Two points seem yet open. Is the nitrogenous matter (albumenoid ammonia of Wanklyn or organic nitrogen of Frankland) destroyed or rendered innocuous? Secondly, is magnesia capable of forming a lake with organic matters to the same extent as the oxides of aluminium and iron?

Among the many interesting facts mentioned in the Appendix, we find that at St. Helens each square mile of surface receives the equivalent of 12,036 tons sulphur. The corresponding figures for London being only 11 tons in winter, and 4.4 tons in summer!

A glance at the specifications of the numerous patents quoted or referred to in this volume will be found exceedingly edifying.

That Prof. Lunge has conferred an immense benefit upon chemical manufacturers and analysts, by the production of this his *magnum opus*, will be gladly admitted by every competent reader. We hope that where this has not already been attended to, the three volumes will be forthwith added to the library of every college, technical school, and no less of every chemist (in the continental sense of the term) in all the English speaking countries.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 19, May 11, 1896.

Nitrates in Potable Waters.—Th. Schlöesing.—The author thinks that as a first test for distinguishing drainage from springs it is sufficient to determine nitric acid and lime. He gives accordingly a tabular view of the quanti-

ties of these two constituents expressed in m.grms. per litre. His determinations of nitric acid are made in 4 litres of water evaporated down to a few c.c. When operating upon the water of the Avre he has always been able to complete this concentration in one and the same 2-litre flask. The precipitate is always more or less yellow, like the dry extract containing the nitrates. The water of the Dhuis is most commonly in the same state as that of the Avre, but the precipitate is of a lighter colour and the dry extract is less yellow. Sometimes it became impossible to evaporate the 4 litres in one flask on account of the violent bumping due to the calcareous deposit, which in such cases was of a pure white, whilst the extract was nearly colourless. In such cases the author divided the water in halves, and boiled them in two flasks until the carbonate was entirely precipitated. He allowed the residues to settle, and evaporated the clear decanted liquids in a third flask.

Condensation of "Black Light."—Gustave Le Bon.—As "black light" possesses several properties which approximate to those of electricity, the author supposed that it might be possible to condense it on the surface of metal plates and then oblige it to traverse the plates so as to act upon photographic plates in darkness, which would place his former experiments in security against all the objections raised against them, especially that of the introduction of light through the chinks of the frames. The author's researches have fully confirmed this hypothesis. He classifies invisible radiations thus:—

X Radiations.—Traverse black paper and organised bodies, but do not traverse most metals; they are neither reflected nor refracted.

Invisible Radiations of Fluorescent Bodies.—Traverse metals as has been shown by D'Arsonval and Becquerel; they are reflected and refracted, and present consequently no property approximating to the X rays.

Radiations arising when Visible Light falls upon Metallic Surfaces.—Our researches show that those radiations traverse neither black paper nor the majority of organised bodies, but traverse a great number of metals. They have also, like electricity, the property of condensing and diffusing themselves on the surface of metals.

Radiations proper to Organised Beings.—Radiations emitted by organisms in darkness, and which enable them to be photographed, as I have shown by operating on ferns, fishes, and various animals. They seem to connect themselves with the radiations of invisible phosphorescence, from which they differ, however, because they do not traverse metallic bodies, those at least upon which I have experimented, especially aluminium.

Action of Hydrobromic Gas upon Thiophosphoryl Chloride.—A. Besson.

Action of Air and of Nitrogen Peroxide upon certain Haloid Compounds of Bismuth.—V. Thomas.—The reactions may be summarised in the following table:—

	Action of Air.	Action of NO ₂ .
BiCl ₃	BiOCl	BiCl ₃ .NO ₂ ; then BiOCl
BiBr ₃	BiOBr	BiOBr
BiI ₃	BiOI; then Bi ₂ O ₃	Bi ₂ O ₃
BiCl ₂	BiOCl	BiOCl

Action of Ethyloxalyl Chloride upon the Aromatic Hydrocarbons in presence of Aluminium Chloride.—L. Bouveault.—The interest of the preparation of the glyoxylic acids of the aromatic series lies in the great ease with which they lend themselves to a crowd of transformations. Claus has shown their easy transformation into substituted phenylglycolic and phenylacetic acids. Gaull has made use of them for the preparation of nitriles by means of hydroxylamin, and the scission observed by Claisen permits us to hope that we may by this means easily prepare the aromatic acids and even the aldehyds.

Novel Method of Separating Naphthylamines.—Marcel Delepine.—Will be inserted in full.

Zeitschrift für Analytische Chemie.
Vol. xxxiv., Part 6.

Wine Statistics of Germany, VIII.—A view of the production of wine in the different districts of the German empire.

On Sodium Sulpharseniate.—Leroy W. McCoy.—The author concludes from his experiments that there exist no proofs for the existence of free orthosulpharsenic acid.

Determination of Nicotin and of Ammonia in Tobacco.—Dr. Richard Kissling.—A criticism of Vendrödi's paper on the "Determination of Ammonia along with Nicotin" which appeared in the *Zeit. Analyt. Chemie*, xxxiv., p. 413.

Determination of Aniline in presence of small quantities of Toluidine, and of Toluidine in presence of small quantities of Aniline.—F. Dobriner and W. Schranz.—Already inserted.

Determination of Moisture in Aniline, Ortho-, and Paratoluidin.—P. Dobriner and W. Schranz.—The authors have ascertained that the moisture of these bases may be determined in a simple manner. It is merely requisite to determine the consumption of bromation-liquid according to Reinhardt (*Zeit. Anal. Chem.*, xxxiii., 89), in equal weights of the undesiccated and the desiccated substances. Let the undried substance consume *a* c.c., the dried *b* c.c.; the moisture *F* may be found by the equation—

$$a : b = (100 - F) : 100,$$

Hence it is indifferent whether the substances in question, independent of the water, are pure, or mixtures of aniline and toluidine, since the proportion of the components is the same in the dried and in the undried substances. Aniline and orthotoluidine can easily be obtained perfectly anhydrous by treatment with ignited potassium carbonate. But if paratoluidin cannot be obtained anhydrous by treatment with fused potassium carbonate at about 50°, and the paratoluidin does not seem to remain quite unaltered after this treatment, at least darker colourations are always obtained. For technical purposes, as commercial paratoluidin contains only minute quantities of aniline, it is sufficient to distil the paratoluidin and to break off the distillation as soon as 10 per cent of distillate have been obtained. The portions remaining in the retort may be regarded as anhydrous.

New Method for Measurements of Temperature.—D. Berthelot.—From the *Comptes Rendus*, cxx., p. 831.

Construction and Examination of Normal Mercurial Thermometers.—J. Pernet, W. Jäger, and E. Gumlich (*Zeit. Instrumentenkunde*).—No details are given.

A Mercurial Thermometer which can be Read from a Distance by an Electrical Arrangement.—M. Eschenhagen (*Zeit. Instrumentenkunde*).—The description of the apparatus is too complicated for insertion.

Electrometric Determination of the Final Point in Volumetry.—R. Behrend (*Zeit. Physik. Chemie*).—If we employ a two-cell element with mercurous nitrate and potassium chloride with mercurial electrodes, we observe a strong indication in an electrometer inserted in the circuit. If we add a solution of mercurous nitrate from a burette to the solution of potassium chloride, the electromotive force becomes smaller, and when all the chlorine is precipitated is almost null. Thus, if we use a silver salt and silver electrodes, the percentage of halogens can be ascertained, and in an ammoniacal solution the percentage of iodine along with the other halogens.

A New Colorimeter.—C. Pulfrich.—Hugo Krüss compares this instrument with his own (*Zeit. Anal. Chemie*, xxxiv., 60), and points out both its advantages and defects.

Spectral Apparatus.—C. Pulfrich and F. L. O. Wadsworth.—The former (*Zeit. Instrumentenkunde*) has devised a spectroscope founded on the principle of light returning

upon itself. The latter describes in the same journal a spectroscope slit with a double movement. No details are here given.

Determination of the Melting and Ignition-point of Explosives.—W. R. Hodgkinson.—(From the *CHEMICAL NEWS*).

MEETINGS FOR THE WEEK.

TUESDAY, 9th.—Medical and Chirurgical, 8.30.
— Photographic, 8.
WEDNESDAY, 10th.—Geological, 8.
THURSDAY, 11th.—Royal, 4.30.
— Royal Society Club, 6.30.
— Mathematical, 8.
FRIDAY, 12th.—Astronomical, 8.
— Physical, 5.

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THE CHEMICAL NEWS

VOL. LXXII, No. 1907

ON THE COLOUR RELATIONS OF ATOMS,
IONS, AND MOLECULES.

PART II.

By M. CAREY LEA.

(Concluded from p. 262).

4.—Classification (continued from Part I.).

ANY attempted classification of the elements is necessarily subjected to a severe test through later discoveries. If the classification is in complete accordance with nature, it must offer suitable places for such new elements as may present themselves later. If it does not do this, it must be more or less artificial.

Mendeleeff's remarkable predictions, and the fact that the elements next discovered found places marked out for them in advance, caused his periodic law to be received with enthusiasm. It so happened that these new elements missed the weak portions of the system. This is now much changed. Within the last year or two, several new elements have been discovered for which the periodic law affords absolutely no place.

This appears to be admitted by Mendeleeff. In an article reprinted in the CHEMICAL NEWS (vol. lxxii., p. 14), he contends that argon must be polymerised nitrogen, and after examining the possible forms that nitrogen might take, he decides in favour of N_3 .

But Berthelot succeeded in combining argon with carbon disulphide, or with its elements, and from this compound he has been able to regenerate argon with all its characteristic properties. This Berthelot justly calls a capital fact. It is scarcely necessary to say that it is quite fatal to the theory of polymerisation just mentioned.

The impossibility of finding a place for argon in the periodic system will become evident from the following considerations:—If its atomic weight should prove to be 19.9, its place will necessarily be between fluorine and sodium. Introduced into the periodic system, it would take its place at the head of the iron group. It is to be remarked that in the periodic system the iron group is a somewhat singular one. It does not include any of the metals which we commonly associate with iron—cobalt and nickel, chromium and manganese. Instead of these, iron is made to form a group with ruthenium and osmium, so that if argon should enter in the periodic system with the atomic weight of 19.9, it would form the head of a group consisting of argon, iron, ruthenium, and osmium. Or of one consisting of A, Co, Rh, and Ir. Or of another, equally anomalous, A, Ni, Pt, Pd.

But argon may prove to have for its atomic weight the number 39.8. For such an element there is absolutely no place in any periodic system. The position required is already occupied by calcium, and a place cannot be made without dislocating all the following groups—a strong argument in favour of the lower figure.

Helium, with an atomic weight of probably 4, offers equally great difficulties. As the old periodic system excludes hydrogen and commences with lithium, with an atomic weight of 7, any element having an atomic weight less than 7 is, like hydrogen, entirely outside of a system which does not recognise the existence of such elements.

In the system which I have proposed, helium, argon (with the atomic weight of 19.9), and their congeners would constitute a group of their own, taking position between the hydrogen group and the lithium group.

In the first part of this paper, I endeavoured to show that the relations of atoms to the visual rays of the spec-

trum might be made the basis of a classification of the elements composed of these atoms, and that such a classification harmonised extremely well with the known properties of the elements. Not that the particular colour exhibited by an atom has for this purpose any importance; the question is simply whether colour is present or absent—in other words, we have to enquire whether a given atom does or does not exercise selective absorption amongst the visual rays. It was there shown that the atoms of all the elements having atomic weights below 48 did not exhibit selective absorption. After this came two elements which I call transitional, because at some valencies their atoms exhibit selective absorption, and at others do not. Next, elements whose atoms at all valencies exhibit selective absorption. Next came a transitional element and then more elements having colourless atoms, and so on through the entire series of elements arranged in the numerical order of their atomic weights.

It is even probable that the distinction so established between these three classes of elements may eventually prove to have a far-reaching significance, and that those elements whose atoms always exercise selective absorption may prove to be differently constituted in some important way from those whose atoms always allow free passage to all the visual rays.

About the same time that the first part of this paper appeared, Julius Thomsen proposed another and a different system of classification (*Zeit. Anorg. Chem.*, ix., 192), to which later he added a supplement (*Ibid.*, x., 155) in reference to my paper, with the object of showing that the elements which I had indicated as possessing coloured ions were found to come together and to occupy certain distinct positions in his series. This, perhaps, may be taken as additional proof of the conformity of the system which I have proposed to the essential characters of the elements.

A few weeks after the first part of this paper was read before the National Academy (April, 1895), M. Lecoq de Boisbaudran brought before the French Academy a note on the subject of the relations of the elements (*Comptes Rendus*, cxx., 20, May 20, 1895). At page 1100 the elements to which his system of nodes and decrements applies are tabulated. They are thirty-one in number, with three additional elements somewhat widely separated from the rest. I observe that all these thirty-one elements, without an exception, belong to my first division, and have atoms that are colourless at all valencies. The three additional elements belong to the transitional class. The elements of the third division—that is, having atoms coloured at all valencies—find no place in his classification. The chances are enormously against this happening fortuitously. The indications from both this and Thomsen's classification are therefore confirmatory of the principle I have endeavoured to establish: that is, that the presence or absence of specific absorption in a certain range of rays is a function of the atomic weight, and is closely related to the constitution of the elements.

In considering the theory of ionic dissociation it is necessary to bear in mind that no rigorous proof has ever been found for it. It remains, therefore, a theory only; a fascinating theory, because it affords beautiful explanations of phenomena which otherwise have none.

There is, however, an important difficulty connected with this theory. The dissociated ions are often spoken of as "free ions," which, in the absence of exterior electrical agencies, static or dynamic, they do not appear to be. It is certain that, after dissociation, the ions continue in some way to influence and control each other. This fact appears in a great number of reactions, of which the following familiar one may be taken as typical:—

If to a dilute solution of ferrous chloride we add dilute hydrochloric acid in excess, completely excluding the air, there will be a considerable dissociation, and the ferrous ions will be in presence of more than enough chlorine

ions, if these were free, to cause at least some portion of the ferrous ions to acquire additional valency and become ferric ions. No change of the sort can be detected. The chlorine ions which would bring about this change are held in check by the hydrogen ions with which they were previously combined. That this is true is shown by removing the hydrogen ions, which is easily done by the addition of nitric acid. Thereupon those chlorine ions which were previously influenced by, and influenced the hydrogen ions, now influence the ferrous ions, converting them to ferric ions.

The facts of osmosis seem to indicate that dissociated ions are mechanically free, inasmuch as the total number of molecules appears to be increased. But the above reaction, which is one of a great number, shows that in a chemical sense they cannot be considered as free.

Those who, like Ostwald, on the contrary, hold that dissociated ions are perfectly free ("Lehrbuch," 2nd Ger. ed., ii., 783), would perhaps explain the above reaction by the asserted principle that plurivalent ions have a tendency to lose a portion of their valency (*Ibid.*, 796 and 801). One of the examples given (p. 796) is that of the trivalent iron ion which, by reason of its tendency to lose valency, may act as an oxidising agent.

This reasoning does not seem to be sound. Whatever may be the tendency of the ferric ion to lose valency, the tendency of the ferrous ion to gain it is still stronger, so that ferrous chloride acts as a powerful reducing agent by reason of the strong tendency of the ferrous ion to acquire additional valency. This tendency of the ferrous ion shows itself in other ferrous salts, and a similar tendency is exhibited by cuprous and stannous salts. In fact, it may be said that most of our powerful reducing agents owe their activity to the tendency of ions to acquire additional valency; consequently, it cannot be admitted that an opposite tendency prevails. And when, in the above-mentioned reaction, we find that ferrous chloride in dilute solution with hydrochloric acid does not take up additional chlorine ions actually present, in spite of its strong tendency that way, we are compelled to believe that the chlorine ions of the hydrochloric acid, though mechanically dissociated, are still held in check by, and hold in check, the hydrogen ions.

In this connection I may refer to some interesting remarks made by Professor Fitzgerald in his recent Helmholtz Memorial Lecture, reported in *Nature* (January 30, 1896):—"It is almost impossible to explain dynamically the assumption that free electrically charged ions wander about in a liquid in a condition at all rightly described as one of dissociation."

And, again:—"The term dissociation, as applied to electrolytes in which this independence of the ions does not exist, is obviously a misnomer. There is said to be an electrical force acting between the various oppositely charged ions into which a dissolved molecule separates, which in some way binds them. Even in dilute solutions this force is very considerable, and must make the condition of charged ions moving independently in the liquid so unstable as to be dynamically impossible unless other important forces operate at the same time."

From these various considerations, the following conclusions may be drawn:—

1. When highly coloured inorganic substances are composed of colourless ions, then if these substances can be brought into solution, the colour wholly disappears. A number of instances are given above, and no exceptions were met with. Much that is important follows from this. It is proved that the ions have become so far separated that they no longer influence each others' vibration periods. For example, antimony pentasulphide is an intensely coloured substance. It dissolves easily in solution of alkaline sulphides, forming absolutely colourless solutions; because the ions of antimony and of sulphur are colourless, and in the act of solution they separate sufficiently to no longer change each others' vibration periods,

without, however, passing out of each others' spheres of influence. The ion theory is the only one capable of explaining this loss of colour; and, on the other hand, the reactions are so exactly conformable to that theory that they constitute a new proof of its correctness.

2. The union of ions, coloured and colourless, gives rise to the most surprising changes of colour. Two similar coloured ions may unite to form a colourless element. Two similar colourless ions may unite to form a strongly coloured element. No black ion is known. There is absolutely no relation traceable between the colour of an ion and that of the element which it forms.

3. The change of colour of an acid indicator placed in contact with an alkali in no way depends upon dissociation: dissociation may result, but the change of colour is independent of it.

4. Selective absorption of the visual rays by an element can never constitute a basis for classification, but the relation of ions to the visual rays leads to a classification which is in absolute harmony with the chemical characteristics of the elements. It may be mentioned that quite recently two chemists, Thomsen and De Boisbaudran, have proposed new systems of classification, in both of which it appeared subsequently that the elements having colourless ions had come together. And in Thomsen's system the same was also true of the elements having coloured ions.

5. Whilst there is good reason for believing that in solution the ions are separated so as to no longer affect each other's vibrations (see Sec. I *supra*), it is also certain that they remain within each other's range of influence, so that they cannot be considered as free. Fitzgerald has shown that this conclusion is in conformity with theory; and experimental evidence has been given above proving that it is also in conformity with fact.

FURTHER NOTES ON THE CHEMISTRY OF THE CYANIDE PROCESS FOR DISSOLVING GOLD.*

By G. A. GOYDER, F.C.S.

Action of Soluble Sulphides in Retarding the Solution of Gold by Potassium Cyanide.

IN consequence of a report that the presence of soluble sulphides in a cyanide solution greatly retards the rate of solution of gold, the following experiments were made to test this point:—50 c.c. of 0.2 per cent cyanide of potassium was run into a bottle, and 1 c.c. of sulphuretted hydrogen water, and shaken. To this solution a gold leaf was added, and the closed bottle was shaken fifteen minutes continuously, the gold leaf not being perceptibly dissolved.† A little oxide of mercury was then added, and quickly dissolved by gentle shaking. Shook continuously for three minutes, during which all the gold dissolved, and a slight precipitate of sulphide of mercury was formed.

A similar experiment was tried with lead acetate as precipitant of the sulphur instead of mercuric oxide. The action of the lead salt was slower, and a decided excess was required, there being no soluble double cyanide of lead and potassium; consequently the sulphide of lead precipitated was accompanied by much cyanide of lead. By using an excess of the lead acetate, however, the normal action of the cyanide was restored. A solution of mercuric chloride was found as effective as the oxide. A trace of an alkaline sulphide was found to act similarly to sulphuretted hydrogen, and to be removable by the same means.

* From the "Seventh Annual Report of the Council of the South Australian School of Mines and Industries."

† Without the sulphuretted hydrogen water the gold leaf would have all dissolved in about three minutes.

Thiosulphates were found not to interfere with the dissolution of the gold. Agitation with lead carbonate for a moderate time does not remove the sulphur.

The action of the sulphur in the above compounds in retarding the dissolution of the gold is evidently due to the sulphur combining with the oxygen present to form oxygen salts, and to gold not dissolving in aqueous cyanide of potassium containing no free oxygen. As shown above, the sulphur is most quickly and economically removed by the addition of mercuric oxide or chloride. The quantity necessary can be readily determined by a few experiments with gold leaf as above, as the gold is not perceptibly dissolved till all the sulphur is precipitated.

Injurious Effect of Iron in the Zinc Boxes.

In conducting some experiments on the precipitation of gold from cyanide solutions, I noticed that strips of iron and zinc coupled at one end caused a considerable loss of cyanide from the solutions without promoting the precipitation of the gold, but rather retarding it, in consequence of the formation of a precipitate, mostly consisting of cyanide of zinc, on the surface of the zinc. Thus, in one experiment, a solution containing 0.183 per cent of zinc potassium cyanide was divided and put into two flasks, one containing a plate of zinc, the other a similar plate coupled to one of iron. After standing eighteen hours the solutions were analysed. That containing the zinc plate only showed no precipitate, and the quantity of soluble cyanide was 0.183 per cent, no loss having occurred, while the solution in the flask with the zinc and iron plates showed a precipitate, and only contained 0.146 per cent of soluble cyanides, showing a loss of 0.037, or one-fifth of the total amount present at the beginning.

In another experiment with a cyanide solution containing gold, the amount of gold left in solution by the zinc plate alone was 0.0026, while that left with the zinc plate coupled to an iron plate was 0.0042, the amount of gold having been the same in each at the beginning. It is, therefore, evident that iron should be altogether excluded from the construction of the zinc precipitating boxes, and the iron-wire screens frequently used should be replaced by perforated zinc, wood, or other suitable material.

I believe it has already been noted in Africa that the presence of iron screens in the zinc boxes is undesirable.

Selective Action.

A good deal of discussion has taken place on the question of the "selective action" of dilute cyanide solutions for gold. Probably this arises from the indefinite nature of the expression, which appears to have been applied in the first case without an explanation of its precise significance.

It may be defined thus:—The selective action of a dilute cyanide solution in dissolving gold indicates that the ratio of gold to base metal dissolved by a dilute cyanide solution is greater than when a strong solution is used, and consequently less cyanide is wasted by using a weak than a strong solution.

As far as I can understand, "selective action" is only claimed for gold as compared with the minerals and gangue with which it is usually associated, and not for artificial products such as zinc, although to a certain extent it might be applied to that metal. There are at least three ways in which aqueous potassium cyanide acts on metallic minerals:—

1. $4\text{KCy} + \text{Cu}_2 + 2\text{H}_2\text{O} = 2\text{KCuC}_2 + 2\text{KOH} + \text{H}_2$.
2. $8\text{KCy} + 2\text{Au}_2 + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{KAuC}_2 + 4\text{KOH}$.
3. $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 + 8\text{KCy} = 2\text{K}_2\text{CuC}_4 + \text{K}_2\text{CO}_3 + 2\text{KOH}$.

In the first case, that of cyanide of potassium acting on native copper, and in the third, in which cyanide of potassium acts on malachite, the velocity of reaction varies directly as the concentration; but in the second,

in which cyanide of potassium acts on gold, the velocity of reaction is principally governed by the amount of free oxygen present, and, as MacLaren has shown, oxygen is more soluble in rather dilute than in strong solutions of potassium cyanide, and does not appreciably diminish in quantity in very weak solutions; therefore the gold will be dissolved more rapidly in rather weak than in strong solutions, and almost as rapidly in very dilute as in moderately dilute solutions. Therefore it is evident that while a very dilute solution dissolves about as much gold by reaction 2 as a strong solution, it would dissolve much less copper or malachite by reactions 1 or 3 than would be dissolved by strong solutions, and the ratio of gold : copper dissolved by the weak solution would be much greater than that of gold : copper dissolved by the strong solution. The fact that copper is also dissolved according to reaction 2 only modifies the ratio, but does not make the two equal.

As pointed out in a previous report, the gold is also dissolved by some of the double salts formed, such as zinc potassium cyanide, in a somewhat similar manner to that described in reaction 2 above, and, as only metals can react with the double salts in this manner, this would tend to still further increase the quantity of gold dissolved by the very dilute solutions.

If the gold were re-precipitated by any of the minerals present, the "selective action" as above described might be more than counterbalanced; but in the absence of salts which would decompose the cyanides there appears to be no re-precipitation of the gold, provided native metals are not present. A sample of crushed copper ore in large excess was mixed in a bottle with a 2 per cent cyanide solution containing 0.0307 of a grain of gold per 100 c.c., and shaken occasionally during a year, at the end of which time the amount of gold was practically the same as at first, amounting to 0.0306 grain per 100 c.c., an intervening assay giving 0.0307 gold. The above test does not of course prove the statement for all minerals; but taken into consideration with the known characteristics of gold cyanides it appears to me to be almost decisive.

THE REDUCTION OF SELENIC ACID BY HYDROCHLORIC ACID.*

By F. A. GOOCH and P. S. EVANS, Jun.

It has long been known that selenic acid is reducible by hydrochloric acid with evolution of chlorine, but the reaction was regarded as more or less uncertain until Petterson showed (*Zeit. Anal. Chem.*, xii., 287) that conditions of action may be secured under which the reduction proceeds so regularly that the chlorine evolved may be estimated iodometrically and taken as the measure of the selenic acid originally present, or of the selenious acid produced. According to this method of determination, it is only necessary to boil a solution of selenic acid in hydrochloric acid of moderate concentration, and if the solution is not too dilute the reduction is obtained in a few moments. Petterson did not, however, fix with exactness the limits of dilution within which a successful determination of the selenic acid may be expected. The object of this paper is to record the results which we have obtained in studying more closely the conditions necessary to an accurate and rapid reduction. We have used in our experiments solutions of selenic acid prepared by oxidising pure, white, re-sublimed selenium dioxide according to the method laid down in a previous paper from this laboratory (Gooch and Clemons, *American Journal of Science*, vol. 1., p. 51) for the quantitative determination of that substance. A portion of the crystalline oxide, approximately 2 grms., was carefully weighed, dissolved in 120 c.m.³ of water

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. 1., Nov., 1895.

containing one-twelfth of its volume of sulphuric acid, and treated with a strong solution of potassium permanganate until the colour characteristic of a distinct excess of that reagent prevailed distinctly over that of the brown oxide of manganese thrown down in the oxidation. The liquid was warmed to about 50° C., bleached by oxalic acid, and the excess of this reagent was destroyed by more permanganate. On account of the tendency of manganous salts, when present in considerable amount in warm solutions containing but little free acid, to react upon any considerable excess of permanganate with the deposition of higher oxides of manganese, it is generally necessary to repeat the bleaching and oxidising process two or three times before the final colour of a slight excess of the permanganate remains in clear solution and indicates the completion of the oxidation of the selenium. Finally, the liquid was filtered, diluted carefully to the volume of one litre, and used as a standard solution.

To determine in a general way the point of dilution at which mixtures of selenic and hydrochloric acids yield chlorine, we submitted various mixtures to distillation in a retort arranged with an inverted condenser (so that the aqueous distillate might be constantly returned to the retort) which was joined to an absorption apparatus charged with a solution of potassium iodide. A current of carbon dioxide was passed through the apparatus during the distillation, to carry forward whatever chlorine might be evolved in the process. The iodine liberated in the absorption apparatus was determined by titration with standard sodium thiosulphate. The results of these experiments are given in the accompanying table.

SeO ₃ present. Grm.	Total volume. C.m. ³	Per cent of HCl, sp. gr. 1.20, by volume.	Time in mins.	Chlorine in terms of the theoretical total.
0.1144	100	5	5	None
"	"	10	"	None
"	"	15	"	About 1%
"	"	20	"	" 7%
"	"	25	"	" 30%
"	"	30	"	" 70%

It is plain that so long as the volume of the hydrochloric acid, sp. gr. 1.20, does not amount to more than 10 per cent of the entire liquid no chlorine whatever is evolved, and that only when the percentage of this acid rises as high as 30 does the chlorine evolved during boiling for five minutes approach the theoretical yield. In the ordinary process of distillation, in which the inverted condenser is not used, the liquid must gradually concentrate and the acid become stronger, so that under such conditions the yield of chlorine in a definite period of time must generally be greater than that obtained in the corresponding experiments of the table. Obviously it is advantageous, in attempting the practical reduction of selenic acid, to begin the distillation with acid of strength sufficient to insure the evolution of chlorine in quantity at the outset, and we have found it best to start with a mixture one-third of which is the strongest aqueous hydrochloric acid, sp. gr. 1.20. With solutions so constituted the reduction goes on rapidly. We have found, however, that care must be taken not to prolong the boiling after the solution reaches a concentration corresponding to hydrochloric acid of half strength; for under such conditions—attained in our experiments either by boiling down mixtures of selenious acid and hydrochloric acid, or by making mixtures of selenious acid containing hydrochloric acid of half-strength—we have found that selenium appears visibly in the distillate, while iodine is set free from the iodide in the receiver. Good results may be expected when the mixture, containing one-third of its volume of the strongest aqueous hydrochloric acid at the beginning, is boiled until all chlorine is expelled, care being taken that the volume of the liquid shall not become less than two-thirds of the original volume.

These are conditions which are easily kept; and we have found that from solutions having a total volume of

75 c.m.³ and containing 25 c.m.³ of the strongest aqueous hydrochloric acid (sp. gr. 1.20), the entire amount of chlorine corresponding to the reduction of 0.2 gm. of selenic acid to selenious acid is liberated in ten minutes. The details of these experiments are given in the accompanying table.

Se = 79.1, O = 16.

SeO ₃ taken. Grm.	Total vol. at the outset.	HCl sp. gr. 1.20 present.	Time in mins.	SeO ₃ found. Grm.	Error.
0.0572	75 c.m. ³	25 c.m. ³	10	0.0568	0.0004—
0.0572	"	"	"	0.0569	0.0003—
0.1144	"	"	"	0.1143	0.0001—
0.1144	"	"	"	0.1137	0.0007—
0.1144	"	"	"	0.1147	0.0003+
0.2288	"	"	"	0.2233	0.0005—
0.2288	"	"	"	0.2279	0.0009—

ON THE QUANTITATIVE DETERMINATION OF HYDROGEN BY MEANS OF PALLADOUS CHLORIDE.*

By E. D. CAMPBELL and E. B. HART.

In the methods heretofore proposed for the quantitative determination of hydrogen in the presence of methane and other paraffins, this element has been estimated from the contraction after complete combustion by explosion with oxygen, or by partial combustion with air and palladium asbestos, or by direct absorption with spongy palladium.

In some cases, where a large amount of gas is available, the mixed hydrogen and paraffins are burned in presence of red-hot copper oxide, the resulting water and carbon dioxide being collected and weighed in the usual manner.

In 1894, F. C. Phillips (*Am. Chem. Journ.*, xvi., 256) proposed the use of palladous chloride, either dry or in solution, as a reagent for the qualitative detection of hydrogen. Phillips has also shown (*Ibid.*, 265—269, and 272) that palladous chloride is reduced by the olefins and by carbon monoxide, which must therefore be removed before testing for hydrogen. The paraffins, he has further shown (*Ibid.*, 262—265), have no action upon palladous chloride, so that hydrogen can be easily detected in their presence. Dr. Phillips proposes the use of dry palladous chloride for the determination of hydrogen, but has not up to the present time overcome the difficulties which he mentions (*Ibid.*, 262).

Thinking it not unlikely that under proper conditions complete absorption of hydrogen might be obtained by means of a suitable solution of palladous chloride, the authors have devised a method based upon this principle, which they have found very satisfactory. This, with Dr. Phillips's permission, they describe below.

A solution of palladous chloride was prepared as follows:—5 grms. of palladium wire were dissolved in 30 c.c. of hydrochloric acid, to which was added 1—2 c.c. of nitric acid. After solution, this was evaporated just to dryness on the water-bath, re-dissolved by adding 5 c.c. of hydrochloric acid (sp. gr. 1.20) and 25—30 c.c. of water, and warming till solution is complete. The solution so obtained was then diluted to 750 c.c., giving a nearly neutral solution, containing about 1 per cent of palladous chloride. This strength of solution was found to be well adapted to the work, and was adopted in our subsequent determinations.

The pipette used in the absorption was the ordinary single Hempel absorption pipette, the only modification being in the clamps which fastened the pipette proper to the stand. In place of the small brass bands generally

* Contributions from the Laboratory of Analytical Chemistry of the University of Michigan. From the *American Chemical Journal*, vol. xviii., No. 4, April, 1896.

used for holding the glass portion in position, three pairs of small screws were substituted, so that the pipette could be easily slipped from between these when desirable, or firmly retained in position by small wires twisted between each pair of screws. In operating, the amount of solution necessary to fill the pipette is first determined and then introduced into the pipette in the usual manner. The gas to be analysed, from which everything but hydrogen, paraffins, and nitrogen had been removed by the usual methods, is then passed into the pipette and followed up by sufficient water to fill the capillary completely. The pipette is then disconnected, after first closing the top with a pinch-cock, removed from the stand, and placed in a water-bath for two hours, at the end of which time absorption will be found complete, unless the amount of hydrogen exceeds 65 c.c., or the pipette has been previously used, in which case a longer time will be required, as will be seen from the experiments cited below.

A pipette should not be used for the absorption of more than about 100 c.c. of hydrogen before re-filling with fresh solution. After absorption is complete, the residual paraffins and nitrogen are passed back, when the residual volume may be measured and paraffins determined by addition of oxygen and explosion in the usual manner. After the pipette has been used for the absorption of about 100 c.c. of hydrogen, the remaining solution of palladous chloride containing precipitated palladium is rinsed into a casserole and then evaporated just to dryness on the water-bath, 5–6 c.c. of hydrochloric acid, and 4–5 drops nitric acid, and a little water are then added and evaporation repeated. The dry palladous chloride so produced is then dissolved by adding 2 c.c. of hydrochloric acid and warming with a small amount of water, and the whole diluted with water to a volume necessary for one pipette full. This solution is then returned to the stock bottle, to be used again when needed.

The accuracy of the above method may be judged from the following experiments. In these experiments all volumes of gases given are those found after reducing to standard conditions, 0° C. and 760 m.m. pressure.

Experiment 1.—

Volume of hydrogen taken = 18.7 c.c.
,, nitrogen ,, = 80.3 ,,

The mixture was passed over 1 per cent palladous chloride, heated to 50° C. overnight; absorption was complete, residue showing 80.3 c.c.

Experiment 2.—

Volume of hydrogen taken = 53.7 c.c.
,, nitrogen ,, = 23.8 ,,

1 per cent palladous chloride was used, and heated in water-bath one hour and thirty minutes. Residue = 23.8 c.c. Absorption complete.

Experiment 3.—To the residue of nitrogen from Experiment 2 was added 26.4 c.c. of hydrogen, and the mixed gases returned to the same solution as was used in Experiment 2. Heated in the water-bath one hour and thirty minutes, it still showed 6.2 c.c. of unabsorbed hydrogen. On again returning the gas to the pipette and allowing it to stand over night in the water-bath, absorption was complete, residue again showing 23.8 c.c.

Experiment 4.—

Volume of hydrogen taken = 1.07 c.c.
,, nitrogen ,, = 52.23 ,,

Heated over 1 per cent palladous chloride in water-bath one hour and thirty minutes, showed absorption of 0.68 c.c. On standing over night in water-bath the absorption was 1.21 c.c.

Experiment 5.—

Volume of hydrogen taken = 1.27 c.c.
,, nitrogen ,, = 70.8 ,,

This was passed over nearly neutral 2 per cent palladous chloride and heated on water-bath over night, showing an absorption of 1.23 c.c.

Experiment 6.—

Volume of hydrogen taken = 60.2 c.c.
,, nitrogen ,, = 18.2 ,,

Passed over nearly neutral 2 per cent palladous chloride, and heated in water-bath one hour and thirty minutes. Residue = 18.2 c.c.

Experiment 7.—Residue from Experiment 6 taken, and 64.4 c.c. of hydrogen added. Mixture returned to same solution as that used in Experiment 6, and again heated in water-bath one hour and thirty minutes. 4.4 c.c. of hydrogen still remained unabsorbed, but on returning the gas to the pipette the second time, and allowing it to stand over night, absorption was complete; the residue measuring 18.2 c.c.

From Experiments 5, 6, and 7 it will be seen that a 2 per cent solution of palladous chloride has very little advantage over a 1 per cent solution. Further experiments showed that with strongly acid solutions absorption was retarded.

The most satisfactory results have been obtained by using a fresh 1 per cent nearly neutral solution for each determination; absorption is then complete in two hours. The pipette can be easily re-filled with fresh solution, the one which has been used being evaporated down and re-dissolved and diluted again. 750 c.c. of solution will be found to be plenty to keep two pipettes in use, the amount necessary for filling an ordinary pipette being about 160 c.c.

VALUATION OF BENZIDINE AND TOLIDINE.

By W. VAUBEL.

THE determination of the contents of the benzidine and tolidine bases is best effected, as a matter of course, with nitrite. In addition, the melting-point may be decisive, as for benzidine it will not lie below 125°, and for tolidine not below 120°. But no result useful for the manufacture of the Congo colouring-matters is obtained by the mere determination with nitrite, since the bases still present as an impurity in benzidine and tolidine, which consist of other diphenyl-derivatives, and are important for the purity of the colours in question, are simultaneously titrated. For the determination of these bases, whose diazo- or tetrazo-compounds yield with naphthionic acid no colours which dye cotton directly, the hydrochloric solution of benzidine or tolidine is precipitated with sulphuric acid or a soluble sulphate, and the base remaining in the solution is determined with nitrite. In various commercial products which I examined in exactly the same manner the following quantities of foreign bases were found:—

	Benzidine.	Tolidine.
1.	0.3 per cent	5.0
2.	0.2–0.3	5.0
3.	0.55	2.8

These figures are, of course, applicable only in the same connection as the solubility of benzidine and tolidine sulphate has to be taken into account.

This is for—Benzidine sulphate, 0.0076 grm. benzidine in 1000 water; tolidine sulphate, 0.03 grm. tolidine in 1000 water.

The error thus arising would not be very considerable; so that the precipitation of the sulphuric acid or the sulphate with benzidine might be elaborated as a volumetric method if the solubility of the benzidine and tolidine sulphate were not considerably increased by the addition of hydrochloric acid. Thus there were obtained for benzidine the following values:—

1000 c.c. water—20 c.c. hydrochloric acid (35 p. c.) dissolve 0.02 grm. benzidine.	
,, ,, 50 c.c. dissolve 0.48 grm. benzidine.	
,, ,, 50 c.c. + 100 grms. sodium acetate dissolve 0.45.	

For tolidine sulphate we have the figures:—

1000 c.c. water—20 c.c. hydrochloric acid = 0.513 grm. tolidin.
" " 50 c.c. = 4.42.

Hence a determination of sulphates or of sulphuric acid can yield by this method merely approximate values, and the figures found above for the impurities of benzidine and tolidine are significant in this connection only. In reality, the amount of foreign bases will be much less.—*Zeitschrift für Analyt. Chemie*, vol. xxxv., p. 163.

ON THE PECULIAR RELATIONS OF SOLUBILITY OF BARIUM SULPHATE.

By R. FRESENIUS and E. HINTZ.

THE authors have made six series of experiments, and summarise the results as follows:—

1. As 4 m.grms. of barium sulphate remain permanently in solution in 400,000 parts of water, whilst 5 m.grms., recently formed, after twenty-four hours occasion a separation, although scarcely perceptible. Hence 1 m.grm. in the nascent state is soluble in about 100,000 parts of pure water.

2. The solubility of barium sulphate in water is most decidedly reduced if the water contains barium chloride or free sulphuric acid, since in their presence 0.5 m.grm. require rather more than 200,000 parts of water for solution, corresponding to the proportion 1 : 400,000 parts; therefore the result to which we are led by the earlier experiments of R. Fresenius.

3. An addition of sulphuric acid decreases the solubility of barium sulphate in water in a rather higher degree than an addition of barium chloride, since the turbidities formed in equal aqueous solutions of barium sulphate formed by sulphuric acid occurred more rapidly and more distinctly than those formed by barium chloride.

4. If barium sulphate separates out of water to which baryta and sulphuric acid have been added in small equivalent quantities, the solution filtered off after twenty-four hours contains in 100,000 parts rather less than 1 m.grm. barium sulphate; for in such filtrates the turbidity occurring on the addition of barium chloride, as of sulphuric acid, rather later than in the solution which had remained clear for twenty-four hours.

(b).—From Series II.

1. As 50 m.grms. barium sulphate remain permanently dissolved in 500 c.c. of an 8 per cent solution of ammonium chloride (at least for seventy-two hours), its solubility in the nascent state in the above-mentioned solution of sal-ammoniac corresponds to the proportion 1 : 10,000 parts.

2. In like manner, its solubility in the solution of ammonium chloride is modified by the addition of barium chloride, and in a far higher degree by an addition of sulphuric acid; for whilst this occasioned a deposition in No. 1 (*i.e.*, in a liquid containing, in 200 c.c., 0.5 m.grm. barium sulphate) there ensued no precipitation, and only a very slight separation in No. 6 (*i.e.*, in a solution containing 5 m.grms. barium sulphate in 200 c.c.). Hence, its solubility in a 10 per cent solution of ammonium chloride in presence of a moderate quantity of sulphuric acid corresponds to the proportion 1 : 400,000; that in presence of a moderate quantity of barium chloride to about 1 : 50,000.

3. Large quantities of ammonium chloride, therefore, do not hinder the precipitation of barium by sulphuric acid, which is always added in excess, whilst they perceptibly interfere with the complete precipitation of sulphuric acid by barium chloride.

From Series III.

1. Whilst 50 m.grms. of barium sulphate remain permanently dissolved in 500 c.c. of an 8 per cent solution of ammonium chloride, this was the case only with 440 c.c. of 2.3 per cent only, for 20 m.grms. corresponding about to the proportion 1 : 22,000. Hence, dilute solution of sal-ammoniac dissolves barium sulphate in a far greater degree than pure water, though not to the same extent as concentrated solutions.

2. In presence of barium chloride, and much more so in that of sulphuric acid, the solubility of barium sulphate decreases considerably in a dilute solution of ammonium chloride, so that the solubility in presence of barium chloride is about 1 : 80,000, and that in presence of sulphuric acid 1 : 400,000.

3. In presence of a moderate quantity of ammonium chloride (2.5 grms. in 100 c.c. of liquid) baryta may be precipitated by sulphuric acid as good as completely; and also sulphuric acid by barium chloride to an extent sufficient for quantitative determinations.

From Series IV.

1. A solution of sodium chloride at 2.3 per cent has a solvent power similar to that of ammonium chloride at 2.3 per cent; therefore, in the former, 440 c.c. remained clear when containing 20 m.grms. barium, corresponding to the proportion 1 : 22,000. On producing 40 m.grms. in the sodium chloride solution there occurred a separation already in ten minutes; whilst in the solution of the ammonium chloride of the same concentration this did not ensue until two hours had elapsed. The solvent power of the latter is, therefore, somewhat greater than that of sodium chloride.

2. On the addition of barium chloride, as well as of sulphuric acid, the same results were obtained as with a solution of ammonium chloride of the same degree of concentration, so that the same conclusions follow in both cases.

Experiments with solutions of sodium chloride at 10 per cent showed that the solvent power of sodium chloride for barium sulphate increases with the concentration as with ammonium chloride. Hence we have a very simple explanation of the fact that muriatic mineral waters not uncommonly contain barium sulphate in solution.

From Series V.

1. As 50 m.grms. of nascent barium sulphate remain permanently in solution in 500 c.c. of nitric acid (at 8 per cent), whilst 100 m.grms. in 600 c.c. of nitric acid at 6.7 per cent give a minimum precipitation only after the lapse of twenty-four hours, the limit of solubility may be assumed at 75 m.grms. in 550 c.c. of nitric acid of 7–8 per cent, corresponding to the proportion 1 : 7300.

2. The solvent power of nitric acid at 10 per cent is considerably reduced by barium chloride, and to a greater degree by sulphuric acid, in an extent increasing with the quantity of the barium chloride or the sulphuric acid, so that from 100 c.c. containing 0.25 m.grm. barium sulphate this body may be eliminated by dilute sulphuric acid, corresponding to the proportion 1 : 400,000; whilst it is separated out by 30 c.c. solution barium chloride only in a solution containing 3 m.grms. in 100 c.c., corresponding about to the proportion 1 : 33,000.

3. Hence, from a 10 per cent solution of nitric acid, baryta can be precipitated as good as completely by a relative excess of sulphuric acid, and sulphuric acid—though less completely—by a relative excess of barium chloride.

From Series VI.

1. The solvent power of hydrochloric acid at 7–8 per cent for barium sulphate is approximately equal to that observed for 7–8 per cent nitric acid, and therefore corresponds approximately to the proportion 1 : 7300.

2. In presence of barium chloride, as well as of sulphuric acid, the solvent action of 10 per cent hydrochloric acid is rather smaller than that of 10 per cent nitric acid, since in 100 c.c. of hydrochloric acid, containing 2 m.grms. barium sulphate, a slight turbidity was occasioned by 30 c.c. solution of barium chloride; whilst in case of nitric acid this does not occur unless 3 m.grms. are present. In 100 c.c. of the hydrochloric acid containing 0.25 of barium sulphate, 4 c.c. of sulphuric acid effected after twelve hours a very slight separation, which did not take place in 10 per cent nitric acid, even if it contained, in 100 c.c., 0.5 m.grm. barium sulphate.

3. It holds good with hydrochloric acid that the solvent power is diminished by barium chloride, as well as by sulphuric acid; the more, the larger is the proportion of the latter.

4. Baryta may be almost absolutely precipitated by an excess of sulphuric acid from 10 per cent hydrochloric, as well as from nitric acid of the same strength. In precipitating sulphuric acid by an excess of barium chloride from such hydrochloric acid, we must remember that in 100 c.c. of filtrate 1 m.grm. barium sulphate remains in solution.—*Zeit. Anal. Chemie*, xxxv., p. 180.

A GENERAL VOLUMETRIC DETERMINATION OF THE METALS PRECIPITABLE BY FIXED CAUSTIC OR CARBONATED ALKALIS.*

By Prof. Dr. RUOSS.

(Concluded from p. 248).

Applications of the Method.

1. *Determination of Alumina in Alums, and of the Free Acid in Aluminic Lyes.*—Mohr, Erlenmeyer, and Löwenstein determine the alumina with litmus as indicator; the two latter authorities employing barium chloride, and, in the case of free acid, with the addition of ammonium-magnesium phosphate—an addition which does not work satisfactorily. Fleischer determines the free acid by adding potassium sulphate, evaporating down, and treating with alcohol. As for the last determination, it may be much more simply effected by methyl-orange. Normal alkali is added until the red changes to orange. For the determination of the former, the solution rendered alkaline is titrated with normal alkali, using phenolphthalein as indicator. If the alum contains salts of ammonium, in presence of which phenolphthalein is not applicable, the ammonia is expelled by boiling with soda, and the liquid is acidified with sulphuric acid, evaporated to dryness, dissolved in water, and titrated.

2. *Determination of Zinc Oxide.*—This determination is effected as follows:—The zinc oxide or zinc carbonate is dissolved in normal hydrochloric acid, and the excess of acid is determined with cupric oxide—ammonia, according to Kieffer's method.

3. *Determination of Hardness of Water.*—This determination with phenolphthalein has the advantage, in comparison of that with oxalic acid, that no filtration and no permanganate solution are necessary, and in comparison with the method of Hehner, that neither filtration nor concentration is required. The procedure is explained by the following examples:—

Measuring Liquids.—Decinormal hydrochloric acid; soda solution, with 4.7364 m.grm. Na_2CO_3 per litre; water, 250 c.c.

Each c.c. of soda solution represents, then, 10 m.grms. per litre; i.e., 1 German degree of hardness and 1 c.c. of hydrochloric acid is equivalent to 1.1174 c.c. of soda solution.

(a) *Permanent Hardness.*—250 c.c. of the water were mixed with 3 drops of phenolphthalein (solution, 1 : 100)

and boiled in a beaker. Soda solution was added by c.c.; at 8 c.c. the liquid was intensely red, even after prolonged ebullition. The liquid was cooled, and hydrochloric acid was added drop by drop, with gentle stirring. The colour was judged by white paper, placed some c.c. beneath the beaker. At 0.6 c.c. hydrochloric acid the liquid was colourless. There were, therefore,—

$$2 \cdot 0.6 \cdot 1.1174 = 1.34 \text{ c.c.}$$

of soda solution to be deducted, and the permanent hardness was therefore 6.7. In the litre there were, therefore, 67 m.grms. lime (calculated as CaO), or 205.8 m.grms. gypsum (calculated as $\text{CaSO}_4 + 2\text{H}_2\text{O}$). If magnesium salts are present, whose carbonate turns the indicator red in the cold, we proceed as for "Precipitation of the Metals as Carbonates."

(b) *Temporary Hardness.*—250 c.c. were mixed in a beaker with five drops of methyl-orange. After adding 7 c.c. hydrochloric acid, the liquid was rose-colour, and after the further addition of 0.4 c.c. soda solution, therefore, there were required, calculated as soda,—

$$7 \cdot 1.1174 - 0.4 = 7.42 \text{ c.c.}$$

soda solution. The temporary hardness is, hence, 7.4 per litre; there are, therefore, 74 m.grms. lime (calculated as CaO), or 132.1 m.grms. calcium carbonate (calculated as CaCO_3).

4. *Determination of Sugar by means of Solution of Copper.*—The original volumetric determination of sugar (Fehling's) has now been superseded by the gravimetric method of Allihn. The weighing of the cuprous oxide, reduced in a current of hydrogen, is now almost universal. Instead of this gravimetric method, some other volumetric processes have been proposed, e.g., the permanganate process, which is not quite free from objections; and that of Gentele with potassium-iron cyanide. In the latter it is not easy, in case of coloured liquids, to distinguish the final reaction. Volhard digests the reduced cuprous oxide with nitric acid, adds sulphurous acid and ammonium sulphocyanide, filters, and determines the excess of ammonium sulphocyanate in the filtrate by means of solution of silver. In order to determine the quantity of copper in cuprous oxide we proceed as follows:—The precipitate, together with the glass or asbestos filter, is digested with nitric acid and then evaporated to dryness with sulphuric acid. (If we have a small paper filter the organic substances formed on its evaporation do not prevent the recognition of the end of the process). The residue, which is now neutral, is dissolved in water, and the copper is determined with alkali or baryta-water, using phenolphthalein as indicator. If the alkali is made up so that its standard is 0.31655, and therefore that 1 litre alkali neutralises 19.896 grm. crystalline oxalic acid, each c.c. indicates 10 m.grm. copper. But if the standard of the lye is V, then—

$$1 \text{ c.c. lye} = V \cdot 31.59 \text{ m.grms. copper.}$$

Allihn's tables then show at once the percentage of sugar.

5. *Determination of Sugar by means of Solution of Silver.*—In this process there is the advantage that silver solutions can be titrated with exceptional sharpness by means of solution of sodium chloride.

6. *Determination of Tannic Acid by Precipitation with Copper Acetate.*—The Schroeder-Lowenthal determination of tannin, which was elaborated by a Commission for deciding on a general method for all determinations of tannin, can, like all determinations of tannin, lay no claim to perfection. The fact that in titration it is by no means indifferent whether the permanganate is added rapidly or slowly involves many circumstantialities which are to compensate the personal factor implicated in working. In particular, the search for the purest possible sort of tannin in commerce, and the determination of its moisture, is a defect which adheres to the method. Even the researches of Kathereiner (*Dingler*, ccxxvii., p. 481) on the process of Carpené-Barbieri showed the solution of permanganate as unsuitable. Only the precipitation of

* *Zeitschrift für Analytische Chemie.*

tannic acid by metallic salts seems to me to allow of an exact determination. It is, of course, necessary to remove the objections raised against it. Amongst the many methods I select that of Fleck, who precipitates with cupric acetate, and calculates the tannic acid from the precipitated copper. The first objection which the Commission made to this method is that the reduction factor of tannin for copper has been stated differently by different authorities. But if we reflect that Eder finds the factor 1.3061, and Wolff as 1.304, the error appears quite insignificant, and due to the great diversity of the different kinds of tannin. The further objection relates to the addition of ammonium carbonate, which has a solvent action upon the copper tannate, whilst in its absence the gallic acid is jointly precipitated. This objection can be removed by omitting this addition, and calculating the copper precipitated before and after the precipitation with hide-powder.

Hence the determination of tannic acid is to be conducted as follows:—

1. A portion of the solution of tannic acid is precipitated with copper acetate. The filtrate is evaporated to dryness with nitric acid and sulphuric acid, dissolved in water, and the copper is determined with phenolphthalein and potassa-lye or baryta-water.

(a). Another portion is shaken up with the dry hide-powder, and filtered after eighteen to twenty hours. In one part of the filtrate the copper is determined as directed in No. 1. The difference of the lye consumed multiplied by a factor gives the quantity of the tannin.

The organic substances, tartaric acid, colouring matters, &c., are destroyed by the evaporation with sulphuric acid and nitric acid, yielding, in part, insoluble blackish brown products. The titration in originally strongly coloured substances, such as decoction of oak-bark, is effected with the same sharpness as in pure tannin, as the red colouration of the indicator shows distinctly. The presence of metallic salts in the original solution is of no importance, as we have to do merely with the difference.

The hide-powder of commerce yields to the filtrate only calcium salts, which on evaporation become sulphate, and do not interfere on titration with potassa-lye or baryta-water.

Liquids for Titration.

1. Per litre, 4 grms. pure copper acetate dissolved in the cold, and filtered if necessary.
2. Potassa-lye, decinormal, or baryta-water.

The solution of tannin is to be diluted to 0.2 per cent, or lower. If the filtrate of the first filtration is cupriferous, the dilution is sufficient.

1. 20 c.c. of solution of tannin are mixed with 20 c.c. solution of copper acetate and a little calcium carbonate (approximately to neutrality) in the cold, and filtered. The filtrate is evaporated to dryness with nitric acid and sulphuric acid dissolved in water, and titrated with potassa-lye or baryta-water, using phenolphthalein as indicator.

2. 100 c.c. of the solution of tannin are mixed with 6 grms. of dry hide-powder and filtered after the lapse of eighteen to twenty hours. With 20 c.c. of the filtrate we proceed as in 1.

The difference of the c.c. of lye consumed in 2 and 1 gives if multiplied by 5.1682, or 51.682, V the number of m.grms. tannin in 20 c.c. of the dilute solution of tannin.

The number 51.682 is obtained from—

$$\frac{79.14}{2} \times 1.3061;$$

1.3061 being the factor taken from the investigations of Eder.

This factor might be established on an investigation of the best qualities of tannin occurring in commerce.

As tannin in alkaline solutions reduces the salts of copper and of silver, we may calculate the quantity of tannin from the quantity of reduced copper or silver before and after the treatment with hide-powder.

NOTICES OF BOOKS.

Argon and Newton: a Realisation. By Lieut.-Colonel W. SEDGWICK (late Royal Engineers), Author of "Force as an Entity," &c. London: W. B. Whittingham and Co. 1896. 8vo., pp. 258.

THE author of the work before us considers that it has distinctly Newton's authority. He informs us, also, that four years before argon was ever heard of he predicted the probable existence of inactive elements, the class to which argon and helium seem to belong. His forecast or prediction is to be found in Chapter III. of his former work, "Force as an Entity," and he was on the eve of pointing it out more formally in an article in the CHEMICAL NEWS (vol. lxxi., p. 139).

As a disciple of Newton he recognises the existence of atoms, hard, solid, and unalterable, under any conditions which now obtain. He agrees with Sir John Herschel and Clerk-Maxwell that the atom has "the essential character of a manufactured article," and he further extends this idea by representing argon and helium as "one of the quarries, as it were, from which the materials for our universe were obtained." Though we do not find any formal deliverance on the question, it can scarcely be doubted that Col. Sedgwick does not regard as possible the decomposition of any of our elements or transformation into each other. He regards man as living in a state of open and formal rebellion, as having left his natural abode—the warm, steamy river valleys—and spread into ungenial regions, where he can exist only by the use of artificial heat, of shelter and clothing. He has further changed his diet. Our author seems not to condemn merely the use of animal food, but of grain and of such vegetable matter as requires to be cooked before use. Naturally he should restrict himself, it would seem, to fruits, nuts, and such roots as can be eaten raw, to succulent shoots and buds.

We perfectly admit that untold misery has been occasioned, not to man alone, but to many of his fellow denizens of the globe, by clearing away the forests, and consequently exposing the mountains and uplands to an alternation of flood and drought. But this work has not been due exclusively or mainly to man's greed or folly. The goat, the rabbit, or rather we might say the rodents generally, have taken a prominent part in laying waste some of the most fertile regions of the earth. The war against the vegetable world is waged to a fearful extent by orthopterous insects. If Col. Sedgwick will carefully consider, we think he will find that man's task of "subduing and replenishing the earth" must turn upon extirpating those creatures which seem to devastate and exhaust it. Were we limited to those regions which we can inhabit without artificial heat and without cooked food, our abode would be very circumscribed.

We must admit that Col. Sedgwick's work is replete with matter not merely interesting, but thought-provoking, though we doubt whether many readers will be prepared to accept all his conclusions.

A Dictionary of Chemical Solubilities, Inorganic. By ARTHUR MESSINGER COMEY, Ph.D. (Professor of Chemistry, Tufts College). London and New York: Macmillan and Co. 1896. 8vo., pp. 515.

A DICTIONARY of solubilities is of immense utility at once in the experimental and in the industrial laboratory. The volume before us is the outcome of prolonged and laborious comparison of most of the standard authorities in inorganic chemistry. We say of *most*, since among the works quoted we find no mention of the works of Watts, of Roscoe and Schorlemmer, and of Würtz. It will further be observed that differences not unfrequently exist among the results given as published by the most

eminent chemists. Thus, barium sulphite is soluble according to Kirwan in 43,010 parts of water, according to Marguerite in 200,000 parts, according to Calvert in 800,000 parts, and according to Fresenius in 400,000 parts. The solubility of lead in distilled water, in water containing carbonic acid, oxygen, presence of gypsum, calcium silicate, magnesium sulphate, old mortar, and sand, lead to great variation in the action of water. For details the readers are referred to the investigations of the Huddersfield Water-Committee of 1886, Messrs. Crookes, Odling, and Tidy, and to the researches of Carnelley (not Cornelley) and Freke published in the *Journ. Soc. Chem. Industry*.

It is very desirable that the solubility of a substance so deleterious as lead, and which has every opportunity of being taken up in public water supplies in consequence of the use of leaden service-pipes, should be placed beyond doubt. Of course a life-time would scarcely suffice for the verification of all the disputed points connected with the solvent action of water upon poisonous matters.

Mr. Comey's work will be recognised as an invaluable laboratory companion; all the more if it were extended so as to include the solubilities of organic bodies.

City and Guilds of London Institute for the Advancement of Technical Education. Report to the Governors, March, 1896. Gresham College, Basinghall Street, London, E.C. 1896.

It has been said that in our modern zeal for education we have begun at the wrong end,—that, instead of furnishing higher instruction to those who needed it and would have turned it to good use, we spent untold millions in forcing elementary education upon those who did not want it, and to whom it has been at best a very doubtful boon. Then, when higher and especially technical training was found to be the real desideratum, we were obliged to appeal to private or casual liberality for the funds required. We are thus competing with ourselves, establishing rival institutions which have substantially the same object. Thus we have the People's Palace, the totality known under the name of South Kensington, the various schools and institutions established by County Councils, &c., as well as the City and Guilds of London Institute, the report of which we are now considering. Now we are not disposed to deny that some of these institutions are doing good work; but are the funds placed at their disposal being laid out to the best advantage? This is a very grave question.

The Council do not omit to put on record the expression of their regret on the death of their late chairman, the Earl of Selborne, to whose energy and devotion much of the growth and prosperity of the Institute is admitted to be owing. The late Professor Huxley is also mentioned as having been an early and valued friend of the Institute.

At the close of last session the diploma of Associate of the City Guilds Institute was granted to forty-seven students, six only of whom had followed the course of chemistry.

A warning is given that, though the electrical industries of the country have opened out a field of employment for well-trained youths, "there have not been wanting signs that the market would soon become over-crowded." It is therefore to be noted with satisfaction that the increase in the day department of the Technical College, Finsbury (210 as against 197 in the previous session), has been more marked in the mechanical and chemical departments than in the electrical department.

Since the close of the first session 431 students have gained certificates, 65 of which are for technical chemistry.

Of the students entered in the evening department, 105 were for chemistry as against 11 in the previous session. Technological examinations were held last year

in 286 towns in the Home Kingdoms, as well as in Sydney, Wellington, Pietermaritzburg, and Bombay.

The total expenditure of the Institute during the past year, in all its branches, has been £30,693 18s. 4d.

This year 46 matriculated third-year students were examined, and 37 were recommended for the diploma of Associate of the Institute; of these six only were for chemistry.

Of the chemical students whose subsequent careers merit notice as real "results," we may mention H. Crompton, Miss A. G. Heath (since dead), R. E. Baker, M. M. Miller, J. Stenhouse, R. W. Sindell, Miss L. E. Walter, E. A. Barnes, W. J. Pope, J. F. Briggs, B. B. Turner, R. L. Jenks, C. Mills, G. C. Jones, O. F. Russell, A. M. Crighton, A. M. Marshall, E. W. S. Schwabe, W. T. Giddon, and E. M. Rich.

The Special Report, by Martin O. Forster, Ph.D., Salters' Company's Research Fellow of the Central Technical College (1895), is well worth a careful study.

We may say, in conclusion, that the City and Guilds of London Institute well deserves the continued and increased support of the public.

Société d'Encouragement pour l'Industrie Nationale, Annuaire pour l'Année 1896. Paris: Chameroi et Renouard.

WE have the yearly calendar of the Société d'Encouragement, with a list of the sittings of the Council, of the financial commission, of the committees of the mechanical arts, the chemical arts, the economical arts, the committee of agriculture, that of commerce, of constructions and the fine arts, and of the editorial commission. There are lists of the members of the Society in general, and of each committee.

The latter portion of the book is occupied with the prizes and medals awarded by the Society in 1895, and the prizes for discoveries and inventions to be offered for the years 1897 and 1898.

The Process Year-Book for 1896. An Illustrated Review of all Photo-Mechanical Processes. Conducted by the EDITOR of *Process Work*. London: Penrose and Co., 8A, Upper Baker Street, W.C. Copyright. 8vo., pp. 168.

THE volume before us is at once satisfactory and disappointing, according to the reader's point of view.

To the artist who looks on photography as a method of obtaining representations of persons, of objects, or scenery, accompanied or eked out by mechanical operations, as admitted by the very word "photo-mechanical," it will be satisfactory as an evidence of decided improvement. For the photo-chemist it will be fraught with a reiteration of former failure. For nearly half a century there has been an active search for true method of photography in colours,—some process for obtaining at once, without any "hand-work" etching and the like can produce on the sensitive plate, the reproduction, *e.g.*, of a sunset-sky in its natural colours, and which shall not be liable to fade. The very fact that, after thousands of experiments, we are little, if any, nearer the mark than in the days of Fox Talbot,—the very fact of such prolonged failure is discouraging, and no less so are the attempts at obtaining coloured results in a round-about and partially mechanical manner. Nevertheless, hope and effort should not be abandoned. Some day objects may be reproduced by a pure photo-chemical process, and we may then bow the hand-work out of court.

Many, very many, of the proofs here inserted as illustrations are admirable as far as anything in mono-chrome can so be called. But in most of the illustrations there is an unpleasant omission,—the scenes, events, &c., should have their names added.

Concerning the fidelity of photography something might be said. On pp. 76 and 77 we have a view of Goredale taken from a woodcut, and a view of the same bit of scenery from a photograph. The latter is the more effective as a picture, but the identity of the two is not beyond question. The second view may have been taken when the river was running low, but the very rocks are dissimilar.

It will be perceived that the "Process Year-Book" is something much more than a trade catalogue. It is a rational survey of photographic art, showing at once its achievements, its short-comings, and its desiderata.

Chemical Experiments, General and Analytical. For Use with any Text-book of Chemistry, or without any Text-book. By R. P. WILLIAMS, Instructor in Chemistry, English High School, Boston; and Author of "Introduction to Chemical Science," "Laboratory Manual," &c. Boston, U.S.A., and London: Ginn and Co. 1895. 8vo., pp. 110.

THE peculiarities of this work, as compared with the very numerous class to which it belongs, is the very extensive use made of contradictions in the technical terms most commonly occurring—names of appliances and of operations. In this manner a considerable saving of room is of course effected, but the book becomes less easy to read and to understand, and mistakes may more readily be made.

A few uncouth terms are due to the same desire for brevity. Thus a glass measure or graduated glass is here named a "graduate." "Fruit jars" are used for making solutions, and must be distinct from beakers, since both figure in the same list of general apparatus. In a list of chemical elements chromium ranks as a non-metal. The final *e* of such words as oxide, chloride, &c., is amputated, and the pronunciation probably undergoes a corresponding change. But we cannot help asking why an author evidently not afraid of innovation does not go a little further? It would be a distinct gain if, instead of fluorine, chlorine, bromine, we were to write fluor, chlor, brom, amputating at the same time the last syllables of cyanogen and of manganese, which the tyro sometimes confounds with magnesia.

If Mr. Williams, in the probable case of a new edition, would take these hints into consideration, he would confer a real boon on chemists beyond mere economy of space.

E. Merck, Darmstadt. Annual Report on the Year 1895.
Published in March, 1896.

THE author or publisher announces that he has added to his factory two new departments—one for the preparation of antitoxin, and the other for the manufacture of remedies from animal organs. With the exception of the so-called anti-vivisectionists and anti-vaccinationists, no one can doubt the potency of certain animal products now being investigated from a therapeutic point of view.

The account here given of the bacteriological department, more especially designed for the preparation of diphtheria antitoxin, is exceedingly interesting and satisfactory. It is less pleasing to find that the wise provision of the German Patent Law, by which its protection was refused to foods and medicines, is, it appears, capable of being evaded.

With rare exceptions Dr. Merck's work is written in idiomatic English, though much of the nomenclature is pharmaceutical rather than chemical.

A compound is here mentioned under the name of *argonen*. We need scarcely say that it contains no argon, and should therefore be re-named as early as practicable.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 20, May 18, 1896.

In the nomination of a member for the Section of Rural Economy, *vice* M. Reiset, deceased, M. Muntz received 38 votes out of the total of 53, and was therefore proclaimed elected.

Emission of New Radiations by Metallic Uranium.—Henri Becquerel.—Will be inserted in full.

Preparation and Properties of Uranium.—Henri Moissan.—Will be inserted in full.

Transformation of the Fat into Carbohydrate in the Organism of Animals not supplied with Food.—A. Chaveau.—By animals not supplied with food the author means especially hibernating animals. He holds that the main fact discovered by Regnault and Reiset gives valuable information on the destination of the fats in physiological energetics. It appears that they are chiefly transformed into potential carbohydrates. We cannot otherwise interpret the fixation of oxygen during the winter sleep with the gradual disappearance of fat and the reconstruction of glycogen and of glucose. But nothing warrants us to conclude that this is a process special to hibernating animals.

On certain Properties of the X Rays traversing Ponderable Media.—C. Maltézos.—If we consider the X radiations as hyper-ultra violet radiations, as there is a tendency to admit, I think that we may explain the fact of the absorbent power of bodies as differing with the density on supposing that the index of refraction is not strictly equal to unity, but that, whilst keeping very near to this value, for all bodies it varies from body to body with the density.

Observations on the Reply of MM. Benoist and Hurmuzescu.—Auguste Righi.—In my communication of April 20th I explained the advantages which we realise on enclosing the apparatus producing the X rays in a conductive case not insulated. These advantages are all peculiar to the case where we study the change which these rays produce on a conductor taken in its natural state. As regards the elimination of the electrostatic forces issuing from the tube, it seems to me that any arrangement and that of MM. Benoist and Hurmuzescu are of the same value. But these physicists believe that this elimination is not complete by my method, and believe that they have found in my paper an assertion in favour of their opinion. This assertion does not exist, as will be seen on reading my communication made to the Academy dei Lincei on May 3rd.

Observations on the X Rays.—T. Argynopoulos.—On experimenting with various fluorescent substances on the X rays I have found that potassium and sodium platino-cyanide and also the potassium and lithium platino-cyanide become much more luminous than the corresponding barium salt. The fluorescence of the former was quite visible at the distance of 5 metres, whilst with the same intensity of the X rays the barium platino-cyanide was visible only at a slight distance.

Tubular Generator for Supersaturation with Ozone.—Gaston Seguy.—The author has devised a new ozonising apparatus intended for industrial, sterilising, and therapeutic applications. The construction of the instrument cannot be made intelligible without the large accompanying illustration.

New Electrolyser.—D. Tommasi.—The advantages presented by this instrument may be summarised as fol-

lows:—Polarisation is totally suppressed; the metal which is precipitated on the disk is removed as it is deposited. The density of the different strata of liquid traversed by the current is everywhere the same, thanks to the continuous rotation of the disk.

Researches on Nickel Cyanide.—Raoult Varet.—A thermo-chemical paper not suitable for useful abstraction.

On a Crystalline Barium Tetrachromite.—E. Dufau.—At the high temperature of the arc chromium sesquioxide combines directly with baryta. The compound formed, $4\text{Cu}_2\text{O}_3\text{BaO}$, scratches quartz, is not attacked by acids, and has at 15° the sp. gr. 5.4.

On the Chloraloses.—M. Hanriot.—The compounds obtained are β -galactochloral, $\text{C}_8\text{H}_{11}\text{Cl}_3\text{O}_6$. It forms, on treatment with acetyl chloride in presence of zinc chloride, a tetra-acetylic derivative. With arabinose the author has obtained arabibromal, $\text{C}_7\text{H}_9\text{Br}_3\text{O}_5$.

Certain Symmetric Aromatic Ureas.—P. Cazeneuve and Moreau.—The compounds in question are diparatolyurea and diorthotolyurea.

Relations existing between the Chemical Constitution of Organic Compounds and their Oxidability under the Influence of Laccase.—G. Bertrand.—The oxidability of the different polyphenols under the influence of laccase seems to depend on the ease with which they can be converted into quinones.

Detection and Separation of the Acid Principles contained in Plants.—Will be inserted in full.

Zeitschrift für Analytische Chemie.
Vol. xxxiv., Part 6.

Proving Measuring Flasks, Pipettes, and Burettes.—Morse and Blacklock (*American Chemical Journal*).—This paper, as well as the following one by J. C. Boor, (*Receuil des Travaux Chimiques des Pays-Bas*), on testing measuring vessels, requires the accompanying figures.

A Blast Lamp.—Henry Brearley.—From the *CHEMICAL NEWS*.

New Gas-burner.—F. Allihn (*Chemiker Zeitung*).—This apparatus differs from that of Muencke merely in the flatter form of its cap.

Regulation of Temperature in Desiccation Boxes.—G. Nass (*Zeit. Angewandte Chemie*).—The description of this apparatus is rather obscure.

A Burette with a Specular Back Wall.—Greiner and Friedrich.—This apparatus is said to admit of more accurate readings. In reading, the operator is to look between the graduation and the numbers through towards the back wall, whilst the light is allowed to fall over his right shoulder.

An Absorption Apparatus for Elementary Analysis.—J. Bredt and W. Posth (*Liebigs Annalen*).—The authors recommend a combination of a calcium chloride tube with the soda-lime tubes. The latter are U-shaped, with two small lateral appendages.

A New Reagent for the Detection of Small Quantities of Hydrogen Peroxide.—A. Bach.—From the *Comptes Rendus* (cxix., 1218).

Determination of the Halogens.—P. Jannasch and K. Aschoff propose a direct precipitation of a solution of thallium sulphate (*Zeit. für Anorg. Chemie*). The procedure is founded on the absolute insolubility of thallous iodide in cold alcoholic water, even in the presence of salts of ammonium and other compounds in the solutions of which thallous chloride remains dissolved. The authors proceed as follows:—About 0.5 gm. of a mixture of sodium chloride and potassium iodide are dissolved in 40 to 50 c.c. of water, and mixed with 50 c.c. of a 20 per cent solution of ammonium sulphate and 30 c.c. of alcohol. There was then added a 4 per cent solution of

thallium sulphate until no further precipitation ensues on a further addition. The yellow thallium iodide thus formed quickly settles on the application of a gentle heat. After standing for twelve hours in the cold, the precipitate, with the aid of a suction-pump, is collected on a weighed filter, and is twice washed with a mixture of 5 parts of ammonium sulphate, 70 parts of water, and 30 parts of alcohol, and finally with alcohol 30 to 50 per cent. The filter, with its contents, was dried at 100° and weighed. To determine the chlorine which has remained in solution, the alcohol is first expelled by heating on the water-bath, the residue diluted with water to about 300 c.c., heated to ebullition, and there are added 10 c.c. of concentrated nitric acid and the quantity of solution of silver necessary for precipitation. The liquid must not be allowed to become cold, to avoid a simultaneous precipitation of silver sulphate. The precipitate is therefore allowed to stand for some hours above the flame; the silver chloride is filtered whilst hot, dried, fused, and weighed. This very simple method yields accurate results. Experiments for a separation of bromine and chlorine in a similar manner were unsuccessful, since thallous bromide is in all cases too soluble. Still thallous bromide is so far insoluble in a solution of ammonium sulphate that this behaviour admits of a useful and characteristic detection of a quantity (not too small) of bromine in presence of much chlorine, and of small quantities of iodine in presence of bromine and chlorine.

Artificial Colouration of Sausages.—M. Marpmann (*Zeit. Angewandte Microscopie*).—The author condemns colouration, even with harmless materials, as it conceals the use of decomposing substances. He cuts a disc of the suspected sausage of 1 c.m. in thickness, comminutes it, and covers it with alcohol at 50 per cent. The cellulose and thin parts are then stained by the pigment present, and this colouration can be recognised under the microscope. Any sausage which, after being covered with alcohol at 50 per cent and standing for two hours at the temperature of a room, still appears coloured, must be regarded as suspicious. Those which lose their colour are not artificially coloured.

Determination of Total Residue from the Evaporation of Water.—P. Mason (*Journ. of Anal. Chem.*)—On account of the hygroscopic character of this residue the author effects the evaporation not in a platinum capsule, but in a weighing-glass. For the removal of the stopper, in case it is held down by a vacuum formed on cooling, the stopper is fitted with a small glass cock.

On Cinnamon Bark.—Rudolf Pfister (*Forschungsberichte über Lebensmittel*).—A botanical-anatomical research.

Microscopic Structure of Clothing.—M. Rübner (*Archiv für Hygiene*).—A photographic method of determining the volumes of the pores, and thus showing the absorbent power of the tissues for moisture and the speed of the movements of air within the clothing. Unequal magnitudes of pores distribute the current of air unequally.

Products of Combustion on the Use of the Auer Burner.—M. Gréhaut.—Already noticed under *Comptes Rendus*, clxx., 349.

Examination of "Prepared Tar."—G. Lunge.—"Prepared tar" is a mixture of the pitch of coal-tar with the less valuable portions of the distillation of coal-tar.

On Tritchell's Method for the Determination of Resin in Soaps.—T. Evan and J. E. Beach.—From the *American Chemical Journal* and the *Journal of Analytical and Applied Chemistry*.

Chinese Insect Wax.—Gehe and Co.—This product has a white crystalline texture, resembling spermaceti. It fuses at 82° to 83° . Its sp. gr. at 15° is 0.926, not 0.970 as was formerly stated.

The Examination of Chloroform.—E. R. Squibb (*Pharm. Rundschau*).

The Law of Noble Metals during Cupellation.—R. Oehmichen. — According to the author's experiments these determinations are accurate when the cupellation is conducted within the limits of temperature at which litharge is formed; 620° (the melting-point of aluminium) is a suitable temperature; 900° is too high, and at it the results are too low.

Volumetric Determination of the Phosphoric Acid of Superphosphates, Soluble in Water.—C. Glaser (*Chemiker Zeitung*).

Determination of Nitrogen in Urine.—H. Moreigne (*Bull. Soc. Chim. de Paris*).—If the volumetric determination of nitrogen is to be applied to the decomposition-liquid obtained on Kjeldahl's principle, the addition of mercury must be omitted.

MEETINGS FOR THE WEEK.

TUESDAY, 16th.—Photographic, 8.

WEDNESDAY, 17th.—Meteorological, 7.30.

Microscopical, 8.

THURSDAY, 18th.—Royal, 4.30.

Chemical, 8. "The Action of Bromine on Pinene in reference to the question of its Constitution," by Prof. Tilden, F.R.S. "Note on Santalal and some of its Derivatives," by A. C. Chapman and H. E. Burgess. "The Explanation of some Anomalies in Thermochemistry—Chloral and Bromal Hydrates," by W. J. Pope. "Further Observations on the Production of Chlorine by Heating a Mixture of Manganese Dioxide and Potassium Chlorate," by Prof. McLeod, F.R.S. "The Rotation of Aspartic Acid," by B. M. C. Marshall. "Occurrence of Quercetin in the Outer Skins of the Bulb of the Onion," and "The Colouring Principle contained in the Bark of *Myrica nagi* (Part I.)," by A. G. Perkin and J. J. Hummel. "Note on some New Derivatives from Camphoroxime," by Dr. M. O. Forster. "Acetylene, its Detection and Ignition in the Air," by Prof. Clowes. Ballot for Election of Fellows.

FRIDAY, 19th.—Royal Institution, 9. "The Utilisation of Niagara," by Thomas C. Martin.

Quekett Club, 8.

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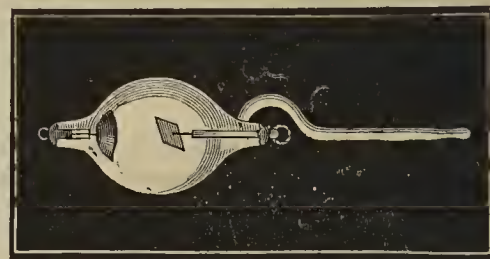
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THE CHEMICAL NEWS.

VOL. LXXIII., No. 1908.

THE BOYLE LECTURE.

DELIVERED BEFORE THE OXFORD JUNIOR SCIENTIFIC CLUB
ON JUNE 12TH, 1896.

By Professor W. RAMSAY, F.R.S.

(ABSTRACT).

The Position of Argon and Helium among the Elements.

THE discovery of argon and helium, like the discovery of carbon dioxide, of oxygen, and of nitrogen, has brought new problems before the scientific world. To afford an idea of the necessary change of views, the lecturer gave a brief account of the more ancient ideas concerning our atmosphere, and the influence of Boyle, Mahon, Hales, Black, Rutherford, Priestley, Scheele, and Cavendish in modifying and converting these primitive notions of the ancients. Portraits of these investigators were thrown upon the screen. The influence of Lavoisier and of Dalton were touched on, and the overthrow of the phlogistic theory—which predicated that combustible substances, when burned, lost a mysterious principle named phlogiston, instead of gaining oxygen—was alluded to.

Passing on to the more immediate subject of his lecture, Prof. Ramsay shortly described the discovery of argon by Lord Rayleigh and himself, and of helium, accidentally found during a search for a clue to guide him in attempting to form a compound of argon. This element, which up to now had been recognised only by the presence of a yellow line in the spectrum of the solar chromosphere, now appears for the first time as a terrestrial substance. Owing to the non-activity and resistance to combination of these newly-discovered elements, the usual method of determining their atomic weights is not available. Hence purely physical methods had to be resorted to: the density of a gas compared with that of hydrogen, the lightest of all known elements, expresses its molecular weight compared with that of a molecule of hydrogen; and, as a molecule of hydrogen is supposed on substantial grounds to consist of two atoms in chemical union, the density is half the molecular weight, compared, as is usual, with the atomic weight of hydrogen. Not all elements, however, possess molecules consisting of two atoms; among those which possess monatomic molecules is mercury, and this is borne out not merely by considerations connected with the formulæ of its compounds, but also by the ratio between the amount of heat required to raise its temperature when pressure is kept constant on the one hand, or, on the other, when volume is kept constant. Heat, according to the modern conception, may be converted into work, and is therefore termed a form of energy; and the heat communicated to mercury gas, provided it be not allowed to expand, is utilised solely in moving its molecules through space, while with other gases some of the communicated heat is employed in causing the atoms to move in some unknown way, in reference to each other, within each molecule. Both argon and helium display the same peculiarity and behaviour, and it is legitimate to conclude, for the same reason, that in their case, too, molecule and atom are identical. Hence the densities of helium and of argon must be half their atomic weights, inasmuch as atomic and molecular weights are the same. This gives for the atomic weights of these elements the number for helium 4.28, and for argon 39.88. The elements arranged in the order of their atomic weights fall into periods, as shown by Mr. John Newlands some thirty years ago. The

atomic weight of argon, however, is almost precisely that of calcium, and it is unusual to find two elements, and beyond experience to find two such unlike elements, with the same atomic weight. It is therefore necessary to seek for some hypothesis which will remove the difficulty. One is, that argon is not wholly composed of monatomic molecules, but contains, among a great majority of monatomic, a few diatomic molecules. Although this supposition has not yet been absolutely refuted, it appears to be highly improbable. Another supposition is, that argon is a mixture of two or more elements with each other. This idea has lately been put to the proof, and negatived. There is no gas in argon lighter or heavier than 19.94 times the weight of hydrogen.

In conclusion, the lecturer alluded shortly to some of the other remarkable properties of these elements; notably their change of spectrum, with change in electric intensity; the great refractivity of helium, and its extraordinary conductivity for electricity; and lastly, he announced that, contrary to all precedent, it diffuses more rapidly than can be deduced from its density. He predicted that such anomalous behaviour would lead to radical changes in our views concerning the minute structure of gaseous matter.

[Prof. Ramsay announced for the first time, in this lecture, that helium diffuses at a rate considerably faster than would be expected from its density, and thus forms the only known exception to Graham's law of diffusion].

DOES HYDROGEN FIND ITS PROPER PLACE AT THE HEAD OF GROUP I. OR AT THE HEAD OF GROUP VII.?

By Professor ORME MASSON, M.A., D.Sc.

1. THE monad valence of H suits either position equally well. The characteristic valence of the halogens is 1, and the tendency of Cl, Br, and I to exhibit higher valence in oxygen compounds is not exhibited by F.

2. The atomicity of hydrogen (H_2) is the same as that of the halogens. So far as the evidence goes, it seems probable that the alkali-metals are, on the contrary, monatomic in the gaseous and dissolved conditions.

3. The gaseous character of hydrogen and its extremely low boiling-point are just what might be expected from an element heading the group F, Cl, Br, I, but the reverse of what might be expected of an element heading the group Li, Na, K, Rb, Cs. If placed in the former position, hydrogen is in close contiguity to all the other older gaseous elements, viz., N, O, F, Cl. To these may probably be added the new gases He and A, which appear to belong to a new Group, VIII.

4. The atomic weights appear to point to Group VII. rather than to Group I., as the proper place for hydrogen, especially if it be permissible to regard helium as a single element of atomic weight 4. [The spectroscopic evidence to the contrary can hardly be regarded as sufficient till supported by other evidence, and at present this is all in favour of the single element view]. In the first place, the difference between the atomic weight of H (1) and Li (7) is only 6, while that between H (1) and F (19) is 18. The difference found between any other two consecutive elements of the same group ranges from about 15 to 20. A difference of 6 would be quite anomalous, but a difference of 18 well within the rule. In the second place, the difference between the atomic weights of two consecutive elements in the same series varies from rather less than 1 to about $4\frac{1}{2}$; and therefore the order $H=1$, $He=4$, $Li=7$ (showing the first members of Groups VII., VIII., and I. consecutively), is quite in keeping with the rule. If, on the other hand, H be grouped above Li, either six gaps for undiscovered elements must be crowded in between $H=1$ and $He=4$, or He must itself find an intermediate position, say above carbon or nitrogen, with gaps on

either side of it. These alternatives are, to say the least of it, improbable. The following table makes these considerations clear:—

Group..	V.	VI.	VII.	VIII.	I.	II.	III.	IV.
Valence	3	2	1	0	1	2	3	4
			H	He	Li	Be	B	C
			I	4	7	9	11	12
	N	O	F	?	Na	Mg	Al	Si
	14	16	19	? 21	23	24	27	28
	P	S	Cl	A	K	Ca	Sc	Ti
	31	32	35.5	? 37	39	40	44	48

5. If H belonged to Group I. it might fairly be expected to have metallic characters, but not so if it belong to Group VII. From Olszewski's experiments it appears that liquid H is not (as formerly reported) physically a metal. Graham's "hydrogenium" argument, based on the metallic characters of the Pd-H "alloy," might be employed to prove the metallic character of oxygen, which "alloys" with molten silver and with solid platinum (occlusion). Where true combination occurs between hydrogen and a metal, it is doubtful whether the product ever exhibits metallic characters. The combustion of Li in hydrogen to form a white saline-looking powder (LiH), recently discovered by Guntz, is very interesting in this connection; for here H behaves towards Li just as do N, O, and the halogens.

6. The only strong argument for endowing H with metal-like characters is that based upon the study of acids and salts. Here we find hydrogen and metals mutually replacing one another, so that the acids are regarded as hydrogen salts. It may be observed, in passing, that the acids do really form a class apart, for they generally differ in the most pronounced manner from true metallic salts of the same radicle. Nevertheless a clear analogy is here proved between the rôle of hydrogen and that of, say, an alkali-metal in one large and important class of compounds, viz., electrolytes.

7. But the study of a different, though equally large and important, class of compounds brings out an equally striking analogy between the rôle of hydrogen and that of chlorine (or fluorine). I allude, of course, to the organic compounds—hydrocarbons and their alcohols, acids, and other derivatives. Here not only do we find hydrogen and the halogens mutually replacing one another, but we find also that this often takes place with no more effect on the general properties of the compound than is produced by the substitution of one halogen for another.

8. It is quite certain, therefore, that the *substitution* argument cuts both ways. An inorganic chemist would be most struck with the analogy between hydrogen and the alkali-metals; an organic chemist with the analogy between hydrogen and the members of the chlorine group. In these circumstances it seems fair to allow other arguments to decide the position of hydrogen in the Periodic classification; and these arguments are all in favour of placing it in Group VII., above F, rather than in Group I., above Li.

ON SOME COLLOIDAL COMPOUNDS OF THE RARE METALS.

By M. MARC DELAFONTAINE.

SOME facts have been known for years showing that the rare metals are capable of forming colloidal (or, as some would say, meta-) compounds. For instance, I described in 1863 a very basic ceric nitrate, the aqueous solution of which very much resembles that of dialysed ferric hydroxide and coagulates upon the addition of a small

quantity of nitric acid. Mr. Bahr discovered a similar thorium compound, and I confirmed that fact.

Mr. Damour made known the rare fact that gelatinous basic acetate of lanthanum turns blue when sprinkled with a little powdered iodine,—as starch does. On resuming and extending some old experiments of mine, on this subject, I ascertained that the metals of the yttrium and didymium groups exhibit properties similar to the foregoing. Here is a brief summary of my experiments and their results:—

Owing to the very great difficulty of preparing *pure* yttrium compounds in large quantity, I first experimented on mixtures of much yttria with little terbia, &c. If, to a moderately strong solution of yttrium acetate, dilute ammonia is added, little by little, there is formed a precipitate which re-dissolves upon stirring. Enough ammonia may be added until the liquid has a faint but decided odour, and turns red litmus blue, and yet no precipitate will be thrown down, even after standing several days. That solution is slightly opalescent; it becomes turbid, and a jelly-like deposit separates when it is boiled; that jelly re-dissolves after cooling, provided the ebullition did not last long.

By dialysis, ammonium acetate was separated. A part of the earthy acetate passed also through the membrane. A clear solution of normal acetate left in contact for many days with yttria, and frequently stirred, gradually dissolves the earth, and makes a colloidal compound identical with that obtained by means of ammonia. After a time, varying from 36 to 72 hours, the remaining fluid exhibited the following characteristics:—

It is transparent, opaline, with a slight fluorescence. It deposits no sediment after standing for a week or more. Its taste is strongly astringent and slightly sweetish. It turns red litmus blue. Its stability is not very great; that is especially the case with long dialysed samples. By boiling, a more or less complete coagulation occurs. The same change will take place at temperatures near 60° C. The solution evaporated at the lowest possible temperature, or in the open air of the laboratory, leaves a transparent gum-arabic-like residue, which does not always *re-dissolve integrally* in cold water. By calcination the solid chars a little, showing that it retains acetic acid.

In small quantity, dilute oxalic acid coagulates the dialysed solution; in larger quantity, at once, it throws down a bulky pulverulent precipitate of ordinary oxalate.

Didymium, lanthanum, and erbium acetate give products similar to that of yttria; the didymium colloidal solution is less stable than that of yttrium.

Some more facts on these compounds will make the subject of a future note. The foregoing facts show that the rare metals can form soluble colloidal compounds entirely comparable to the so-called soluble alumina and dialysed peroxide of iron, which also retain strongly a small proportion of their original acid.

Linebarger's experiments on colloidal tungstic acid, and supported by other researches, suggest that the above-described substances are highly condensed hydrates. Whether the small proportion of acetic, nitric acid, or chlorine left in the final products, is a mere impurity not separated by dialysis or an inherent component of the molecule—a part of a colloidal or meta-salt—does not seem to be an answerable question at present.

South Division High School, Chicago, U.S.A.,
June 1, 1896.

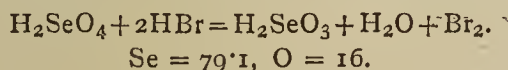
Royal Institution. — A General Monthly Meeting of the Members of the Royal Institution was held on June 1st, Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, presiding. The following were elected Members:—William Phipson Beale, Q.C., F.G.S.; Miss Esther Bright; Edward Ball Knobell, Treas. R.A.S.

THE REDUCTION OF SELENIC ACID BY POTASSIUM BROMIDE IN ACID SOLUTION.*

By F. A. GOOCH and W. S. SCOVILLE.

It has been shown in previous papers from this laboratory that potassium bromide may be used with good effect in presence of acid and under well-defined conditions as a reducer of arsenic and telluric acids. This paper gives the results of similar experiments made to test the interaction between the bromide and the selenic acid.

In our experiments we have used selenic acid carefully prepared by oxidising pure, white, re-sublimed selenium dioxide by means of potassium permanganate in the manner described (*Am. Journ. Sci.*, 1, 400; *CHEM. NEWS*, lxxiii., 273). When intermixed with sulphuric acid and potassium bromide, selenic acid liberates bromine in proportion to the excess of acid, the bromide, and the elevation of the temperature. When such a solution is boiled the bromine is evolved and may be collected in potassium iodide contained in any appropriate receiver, and the iodine thus set free may be determined by standard sodium thiosulphate and taken as the measure of the bromine distilled. We have found an apparatus previously used in this laboratory in similar work (made by sealing the exit tube of a Voit wash-bottle, used as a retort, to the inlet-tube of a Drexel wash-bottle used as a receiver, with a set of Will and Varrentrapp absorption bulbs sealed to the outlet-tube of the receiver, to serve as a trap) extremely convenient in the distillation process, and a current of carbon dioxide passed slowly through the apparatus aids greatly in carrying the bromine to the receiver and in promoting quiet boiling. We find that the applicability of the reaction to quantitative purposes turns upon the adjustment of the proportions of the reagents used. The following table contains the results obtained by varying the relative amounts of acid and bromide and the time of boiling. The selenium trioxide recorded as found is calculated upon the assumption that selenious acid is the product of the reduction according to the equation—



	SeO ₃ taken as H ₂ SeO ₄ . Grm.	H ₂ SO ₄ of half- strength. taken. C.m. ³ .	KBr taken. Grm.	Initial volume. C.m. ³ .	Final volume. C.m. ³ .	SeO ₃ found. Grm.	Error. Grm.
1.	0.1145	5	1	60	25	0.1140	0.0005—
					15	0.1193	0.0048+
2.	0.1145	5	5	60	30	0.1134	0.0011—
					23	0.1184	0.0043+
3.	0.1145	10	1	60	27	0.1134	0.0011—
					23	0.1141	0.0004—
4.	0.1145	20	1	60	35	0.1152	0.0007+
5.	0.1145	20	1	60	35	0.1144	0.0001+
6.	0.1145	20	5	60	45	0.1172	0.0027+

From these results it is apparent that the amount of iodine set free in the receiver is dependent upon the proportion of the bromide, the strength of the acid, and the degree of concentration during the distillation. When the proportions of sulphuric acid, potassium bromide, and selenic acid are favourable, the bromine liberated is removed rapidly to the distillate, leaving the residue perfectly colourless, but as the distillation is continued the liquid residue again takes on colour and more iodine is set free by the action of the distillate upon a clear solution of potassium iodide, while selenium is plainly visible in the receiver. When the amount of potassium bromide is large, its effect is to retain bromine in the liquid so obstinately that no period of colourlessness intervenes before the second stage of colour arrives; when its amount is small while that of the sulphuric acid is also small,

the reduction of the selenic acid and the evolution of the bromine progress slowly; and when the amount of bromide is small, while that of the acid is comparatively large, the interval of colourlessness is prolonged. The proportions which we found best in handling 0.25 gm. of selenic acid, or less, are an initial volume of 60 c.m.³ containing 20 c.m.³ of sulphuric acid of half-strength with 1 gm. of potassium bromide. Under these conditions we find, as in Experiments 4 and 5 of the previous table, that the reduction is almost theoretically exact when the distillation is continued until the re-colouration of the boiling liquid is distinctly recognisable; and this point corresponds in practice very closely to a concentration of volume to 35 c.m.³. In the following table are gathered the results of further experiments in which these conditions of action were preserved:—

SeO ₃ taken as H ₂ SeO ₄ . Grm.	H ₂ SO ₄ of half- strength. taken. C.m. ³ .	KBr taken. Grm.	Initial volume. C.m. ³ .	Final volume. C.m. ³ .	SeO ₃ calculated. Grm.	Error. Grm.
0.0590	20	1	60	35	0.0588	0.0002—
0.0590	20	1	60	35	0.0591	0.0001+
0.0614	20	1	60	35	0.0616	0.0002+
0.0614	20	1	60	35	0.0607	0.0007—
0.1180	20	1	60	35	0.1177	0.0003—
0.1180	20	1	60	35	0.1180	0.0000
0.1534	20	1	60	55	0.1527	0.0007—
0.2349	20	1	60	35	0.2350	0.0001+

It is plain from these results that, if the conditions of action which we have indicated are observed, the reduction proceeds with regularity sufficient to warrant the use of the reaction as an analytical process.

PHOTOMETRIC METHOD
FOR THE
QUANTITATIVE DETERMINATION OF LIME
AND SULPHURIC ACID.

By J. I. D. HINDS.

THE want of a rapid method of determining with a close approximation the amount of lime and sulphuric acid in drinking water led me to the study of the opacity of fine white precipitates suspended in water. I precipitated in weak solutions lime with ammonium oxalate, and sulphuric acid with barium chloride, then measured the height of a column of the liquid containing the precipitate through which the flame of a common candle was just invisible. I expected only a rude approximation, but to my surprise I found that, between certain limits, an accuracy is attainable equal to that of the ordinary volumetric method.

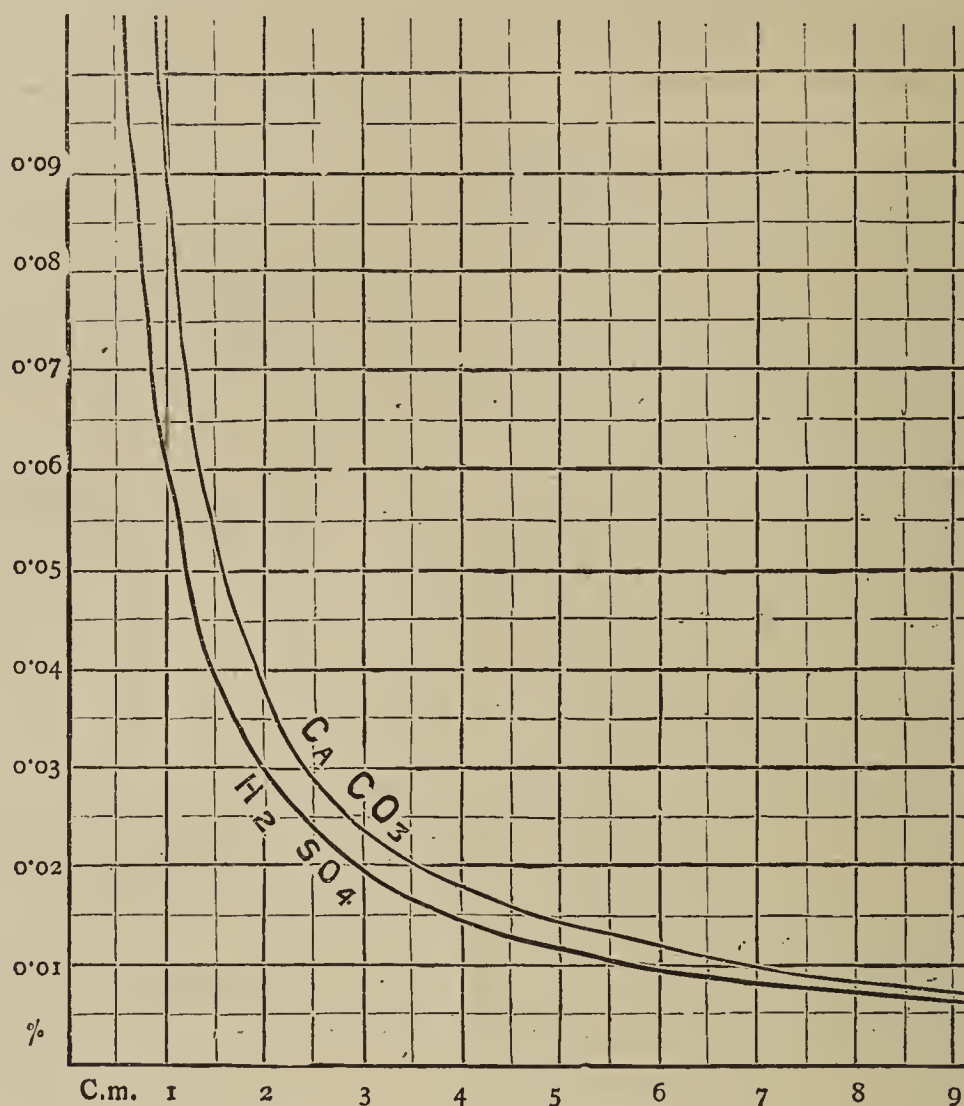
Apparatus.

The only apparatus needed is a cylinder graduated from the bottom in centimetres and tenths. The cylinder should have a plain polished bottom, like Nessler cylinders, and should have a lip at the top. The one I use was made by Eimer and Amend, New York. It is 4 c.m. wide and 20 c.m. high. The graduations run to 18 c.m. This cylinder, however, is not absolutely necessary. A common beaker may be used and the depth of the liquid measured with a small ruler.

The Method.
For Sulphuric Acid.

To determine the values for sulphuric acid I used a decinormal solution whose actual strength was 1 c.c. = 0.00492 gm. H₂SO₄. I took 10 c.c. of this solution, acidulated it slightly with hydrochloric acid, and diluted it to 200 c.c. Of this solution I took 40 c.c., which contained 0.00984 gm. H₂SO₄. To this I added enough solid barium chloride to effect complete precipitation, mixed thoroughly by pouring from beaker to cylinder and

* Contributions from the Kent Chemical Laboratory of Yale College. From the *American Journal of Science*, vol. 1., Nov., 1895.



Equations.

$$\text{H}_2\text{SO}_4 \quad y = \frac{0.0590}{x}$$

$$\text{CaCO}_3 \quad y = \frac{0.0642}{x - 0.3}$$

back, then measured the depth of the column through which the flame was invisible. I then added successive portions of 10 c.c. water, taking the measurement after each addition. The measurement is made as follows:—Hold the cylinder some 12 inches above the burning candle; looking downward through the cylinder, pour in the liquid until the image of the flame just disappears, then read the depth of the liquid. By applying the lip of the beaker to the lip of the cylinder a very gentle stream may be made to flow in. The reading should be made two or three times so as to be sure to read the proper tenth. It is well also to enclose the cylinder in the hand, cutting off the surrounding light, so that the observation may be more accurate.

In this way I obtained the following series of determin-

P.c. H_2SO_4 .	y .	C.m.	C.m.	C.m.	C.m.	x .	xy .
1.	0.0246	2.4	2.4	2.4	2.4	2.4	0.0590
2.	0.0197	3.0	3.0	3.0	3.0	3.0	0.0591
3.	0.0164	3.6	3.6	3.6	3.5	3.575	0.0586
4.	0.0140	4.2	4.2	4.2	4.2	4.2	0.0588
5.	0.0123	4.7	4.8	4.8	4.7	4.75	0.0584
6.	0.0109	5.3	5.4	5.4	5.3	5.35	0.0583
7.	0.0098	5.8	5.9	5.9	5.8	5.85	0.0573
8.	0.0089	6.4	6.4	6.4	6.4	6.4	0.0570
9.	0.0082	6.9	6.9	6.9	6.9	6.9	0.0566
10.	0.0076	7.4	7.5	7.5	7.5	7.475	0.0568
11.	0.0070	8.0	8.0	8.1	8.1	8.05	0.0564
12.	0.0066	8.6	8.6	8.7	8.7	8.65	0.0570

ations. The strength of the solutions is expressed in per cent of H_2SO_4 , and is represented by y . Column 1 gives the number of the solution; col. 2 the per cent of H_2SO_4 ; cols. 3, 4, 5, and 6 give the depths of the liquid in c.m. and tenths for four series of observations; col. 7 contains the means of these depths, expressed also by x ; col. 8 contains the products of these means by the percentage, represented also by xy .

I found that the continued agitation and dilution of the solutions seemed to increase the opacity, though very slightly. So I made another series with solutions more dilute, with the following result.

Second Series.

P.c. H_2SO_4 .	y .	C.m.	C.m.	C.m.	C.m.	x .	xy .
1.	0.0098	6.1	6.1	6.0	6.1	6.075	0.0595
2.	0.0089	6.6	6.7	6.6	6.6	6.625	0.0589
3.	0.0083	7.2	7.3	7.3	7.3	7.275	0.0597
4.	0.0075	7.9	7.9	7.9	7.9	7.9	0.0592
5.	0.0070	8.5	8.5	8.4	8.4	8.45	0.0591
6.	0.0066	9.0	9.1	9.1	9.1	9.075	0.0598
7.	0.0061	9.6	9.7	9.7	9.7	9.675	0.0590
8.	0.0058	10.2	10.2	10.2	10.2	10.2	0.0591
9.	0.0055	10.8	—	—	10.8	10.8	0.0594

Mean value of xy 0.0593

Mean value of xy for the first six of

First series 0.0587

Mean of the two 0.0590

We observe that the product xy , that is the number obtained by multiplying the per cent of sulphuric acid in the solution by the depth of the column through which the flame is just invisible, is a constant, and that the curve made by taking the one as the ordinate and the other as the abscissa is an hyperbola referred to its asymptotes, of which the equation is—

$$xy = 0.0590:$$

This is represented by the lower curve in the accompanying diagram. Solving the equation for y , we have—

$$y = \frac{0.0590}{x}$$

To find the amount of sulphuric acid in any solution, observe the value of x , divide it into 0.0590; the quotient will be per cent. Or remove the decimal point three places to the right and we have parts in 100,000. For example, suppose the depth observed is 5.0 c.m.; the quotient is 0.0118. The solution therefore contains 0.0118 per cent of sulphuric acid, or 11.8 parts in 100,000.

For SO_3 the equation is—

$$y = \frac{0.0482}{x}$$

In the above example the amount of SO_3 is 0.00965 per cent, or 9.65 parts in 100,000.

Probable Error.

To determine the probable difference between the observed and computed values, we may compare the second set of observations above with the percentages calculated from the equation. In the following table the first column contains the observed depths of the liquid; the second gives the actual strength of the solution used; the third gives the numbers calculated by the equation; the fourth contains the difference; and the fifth the square of the difference between the numbers of the two preceding columns. This difference is represented by v .

C.m.	Per cent used.	Per cent calculated.	v .	v^2 .
6.0	0.0098	0.0098	0.0000	0.00000000
6.6	0.0089	0.0089	0.0000	0.00000000
7.3	0.0082	0.0081	0.0001	0.00000001
7.9	0.0075	0.0075	0.0000	0.00000000
8.5	0.0070	0.0069	0.0001	0.00000001
9.0	0.0066	0.0065	0.0001	0.00000001
9.7	0.0061	0.0061	0.0000	0.00000000
10.2	0.0058	0.0057	0.0001	0.00000001
10.8	0.0055	0.0055	0.0000	0.00000000

$$\text{Sum } \Sigma v^2 \dots \dots \dots 0.00000004$$

By the method of least squares, the probable error, r , is obtained by the equation—

$$r = 0.6745 \sqrt{\frac{\Sigma v^2}{n-q}}$$

in which n = the number of observations, in this case nine, and q the number of constants in the equation, in this case one. The equation becomes—

$$r = 0.6745 \sqrt{\frac{0.00000004}{8}} = 0.00005$$

The probable difference, then, is 0.00005 per cent, or one part in 2,000,000.

(To be continued).

Northern Polytechnic Institute, Holloway. — Mr. Thomas Ewan, B.Sc. (Viçt.), Ph.D. (Munich), Assistant-Lecturer in Chemistry, The Yorkshire College, Leeds, has been appointed Chief Assistant in the Chemical Department in this Institute.

ACIDIMETRIC ESTIMATION OF VEGETABLE ALKALOIDS. A STUDY OF INDICATORS.*

By LYMAN F. KEBLER.

THE titration of alkaloids with volumetric acid solutions has been evolved from the study of the basicity of the alkaloids on the one hand, and from their behaviour with indicators on the other. The method appears to have been developed somewhat spasmodically from quite an early period. As early as 1846 M. Schlössing (1846, *Comptes Rend.*, xxiii., 1142; 1847, *Ann. Chim. Phys.* [3], xix., 230; *Chem. Gaz.*, v., 41; *Am. J. Pharm.*, xix., 68) proposed the method, and applied it to the titration of nicotine with a view of establishing its equivalent, using sulphuric acid and litmus in his work. Sixteen years later the work was taken up by Wittstein (1862, *Vierjahrschr. Prakt. Pharm.*, xi., 351), who was followed by F. M. Brandl (1864, *Vierjahrschr. Prakt. Pharm.*, xiii., 322), Liecke (1865, *Mittheilungen des Hannov. Gew.-Ver.*, p. 160; *Ding. Poly. J.*, clxxviii., 235; *Polyt. Notizbl.*, No. 20; *Zeits. Anal. Chem.*, iv., 492), Kosutany (Kosutany, "Anal. Bestim. einiger Bestandth. d. Tabakspflanzen. Diss. Altenburg, Hungary"), and G. Dragendorff (1874, "Chem. Werthbestin," pp. 42 and 55; see also "Plant Analyses," 1884, Eng. ed., pp. 63 and 188). Up to this time nicotine and conine were the only alkaloids operated on, and litmus the only indicator employed. In 1879 L. van Itallie (1879, *Nederland. Tydschr. v. Pharm.*, Jan.; *Analyst*, xiv., 118) extended the work to several other alkaloids, using lacmōid as indicator. A. W. Gerrard (1882 and 1884, *Year-book of Pharm.* pp. 401, 447), a few years later, employed litmus and phenolphthalein in titrating the alkaloids of belladonna. From the contributions of O. Schweissinger (1886, *Pharm. Centralhalle*, xxvii., 492), who used cochineal as indicator, and those of E. Dieterich (1887, *Pharm. Centralhalle*, xxviii., 21; *Pharm. J. Trans.* [3], xvii., 888; *Am. J. Pharm.*, lix., 179) and P. C. Plugge (1887, *Arch. d. Pharm.* [3], xxv., 45, 49; *J. de Pharm. et de Chim.* [5], xv., 571; *Ber. d. Chem. Ges.*, xx., 148; *J. Chem. Soc.*, lii., 621) we may ascribe the impetus which the titration of alkaloids with volumetric acid solutions received at the beginning of the present decade.

The method had been gaining ground rapidly when several most valuable communications appeared by C. C. Keller (1892, *Schweiz. Wochenschr. f. Chem. u. Pharm.*, xxx., 501, 509; *Am. J. Pharm.*, lxxv., 78; 1893, *Schweiz. Wochenschr. f. Chem. u. Pharm.*, xxxi., 473; *Ztschr. Oesterreich-Apoteker*, xlvii., 563, 586; *Am. J. Pharm.*, lxxvi., 42), of Zurich, since which great improvement has been made.

In volumetric analysis, the first question demanding attention is a suitable indicator or delicate end reaction.† The object of this communication is to present the results of a study of five indicators in titrating alkaloids, thinking perhaps it may be of some service in formulating systematised methods of analysis in alkaloidal chemistry. The discordant results of analysis often obtained by different chemists operating on the same sample are greatly to be regretted. It is the writer's opinion that the discrepancies are chiefly due to differences in *modus operandi*, to defective apparatus, and, in volumetric analysis, to different end reaction tints arbitrarily assumed by each worker.

In order to eliminate the factors of uncertainty as completely as possible, the methods of operation were carefully written out and closely adhered to in all the work. The burettes and a pipette were carefully calibrated in order to ascertain the necessary factor for correction.

* Read at the Springfield Meeting. From the *Journal of the American Chemical Society*, vol. xvii., No. 10, October, 1895.

† Alkaloids, generally, are neutral to phenolphthalein; consequently it cannot be employed in titrating alkaloids directly. It is available for indirect titrations, i.e., estimating the amount of acids combined with an alkaloid in its neutral salts.

The method of calibration was as follows:—Each burette and pipette was exactly filled to the zero mark with distilled water, at 15° C. and 10 c.c., delivered into a tared weighing flask and weighed, then the next 10 c.c. were treated in the same manner, and so on until the entire capacity of each was tested. A glass-stoppered cylinder was also standardised. All efforts to standardise a litre flask were thwarted. A large balance sufficiently sensitive to do the work satisfactorily could not be found.

In titration the personal equation plays an important part. Authorities are not agreed on end reaction tints, each operator relying on his own judgment. The writer thinks it correct to titrate to the point where a different colour from the initial colour is developed. In order to obtain standard end reaction tints for alkaloids it will be necessary to prepare some absolutely pure alkaloid; treat a molecular quantity of the alkaloid with an equivalent of the acid in question to form a neutral salt, then add one drop more of the decinormal acid for an acid colour reaction. For alkaline tints add one drop of the centinormal alkaline solution to a solution of neutral alkaloidal salt, theoretically prepared.

In this work the writer titrated from acid to alkaline solutions as follows:—Brazil wood, from yellow to onion-red, the purple ultimately fading to this; cochineal from yellow to bluish red; hæmatoxylin from yellow to brown-orange; litmus from red to onion-red; and methyl orange from red to straw-yellow.

The indicator solutions were prepared according to the most approved processes. Cochineal and litmus were prepared according to the specifications of Sutton's "Volumetric Analysis," sixth edition. Phenolphthalein, 1 grm. dissolved in 1 litre of 50 per cent alcohol. Hæmatoxylin, well crystallised, 1 grm. dissolved in 100 c.c. of strong alcohol. The method best suited for preparing the Brazil wood solution is to place 3 grms. of the wood into a casserole, add 10 c.c. of distilled water, boil gently for a few minutes, cool, and filter. A freshly prepared solution has given the writer the most satisfactory results. Methyl orange, 1 grm. dissolved in 1 litre of distilled water. Considerable difficulty was experienced in obtaining even a fairly satisfactory product of methyl orange. The method proposed by Mr. B. Reinitzer (1894, *Ztschr. Angew. Chem.*, 547, 573; *CHEM. NEWS*, lxx., 225, 239, 249) for preparing the litmus solution did not come to the writer's notice until considerable work had been done with the solution prepared as above.

In titration the following quantities of the several indicators were employed:—Methyl orange, Brazil wood, cochineal, and phenolphthalein, 5 drops each; litmus 10 drops, and hæmatoxylin 3 drops.

The standard solution employed in this investigation, from which the exact strength of the other volumetric solution was determined, was a solution of normal sulphuric acid. This solution was prepared from data obtained by the several methods; titration against pure anhydrous sodium carbonate, using the above indicators; precipitation as barium sulphate and Weinig's (1892, *Ztschr. Angew. Chem.*, 204; *Analyst*, xvii., 99) process. After some experimentation it was found that Weinig's method gave the most satisfactory results. The method is simple, and yields very concordant results. The following are the data obtained from an approximately normal sulphuric acid solution with the above methods:—

Indicators and methods.	No. of c.c. of acid solution required per 10 c.c. of normal sodium carbonate.	Grms. of SO ₃ in 10 c.c. of the acid solution.
Brazil wood	9.50	0.4211
Hæmatoxylin	9.54	0.4192
Cochineal	9.50	0.4211
Litmus	9.50	0.4211
Methyl orange	9.50	0.4211
Phenolphthalein	9.45	0.4216
Weinig's method	—	0.4247
Barium sulphate method	—	0.4200

Due precaution was taken to boil the solution thoroughly with the indicators requiring it. With solutions of the above strength it was impossible to detect any difference in the sensitiveness of most of the indicators.

With the normal sulphuric acid solution a normal solution of pure potassium hydroxide was standardised. From the normal sulphuric acid solution and normal alkaline solution there were prepared, respectively, a decinormal acid solution and a centinormal alkaline solution. The two solutions thus prepared were carefully titrated against each other, employing the above indicators, with the following results:—

Indicators.	No. of c.c. of normal sulphuric acid.	No. of c.c. of centinormal KOH required per 10 c.c. of decinormal H ₂ SO ₄ .	
		LaWall.	Kebler.
Phenolphthalein ..	10	101.80	102.00
Brazil wood	10	99.56	100.00
Cochineal	10	100.58	99.80
Hæmatoxylin	10	99.76	100.00
Litmus	10	99.97	99.60
Methyl orange	10	92.67	98.53

My associate, Mr. LaWall, took up a portion of the work, which he executed independently, using, however, the same solutions and apparatus that the writer employed. The above, and all subsequent results, are the average of duplicate, triplicate, or more titrations.

The titration of pure alkaloids, as found in the market, was next undertaken. With quinine and codeine the following method was used:—Two grms. of the alkaloid were placed in the cylinder, dissolved in alcohol, and diluted up to 100 c.c. with alcohol. To 10 c.c. of this solution and the requisite quantity of indicator contained in a suitable beaker, the decinormal acid solution was added to slight excess, agitated, allowed to stand a few minutes, the sides of the beaker well washed down with distilled water, adding about 40 c.c., and the excess of acid titrated back with the centinormal alkaline solution.

With alkaloids not freely soluble in alcohol the following procedure was adopted:—Two grms. of the alkaloid were placed into a 200 c.c. beaker, 75 c.c. of decinormal acid added, the contents of the beaker warmed on a water-bath, and occasionally agitated until the alkaloid was dissolved. The beaker and contents were then cooled, the contents transferred to a 100 c.c. cylinder, the beaker carefully rinsed with several successive portions of water, transferred to the 100 c.c. cylinder, and finally made up to 100 c.c. with water. Each 10 c.c. contained two-tenths of a grm. of alkaloid and 7½ c.c. of decinormal acid solution. After adding the requisite amount of indicator to 10 c.c. of the alkaloidal solution, and diluting up to about 50 c.c., the excess of acid was carefully re-titrated. Two or more titrations were made in every case, with the same solution and indicator, by adding to the solution just finished another portion of the decinormal acid solution, and re-titrating with the centinormal alkaline solution, taking finally the average reading.

The above methods of titration and preparation of solutions were employed with several pure alkaloids. The results are tabulated below.

Indicators.	Quinine.		Strychnine.		Morphine.		Codeine.	
	LaWall.	Kebler.	Kebler.	Kebler.	Kebler.	Kebler.	Kebler.	Kebler.
Brazil wood ..	99.90	101.97	99.36	98.93	95.75			
Cochineal ..	105.56	102.54	103.20	99.08	97.09			
Hæmatoxylin ..	99.81	103.37	100.03	98.17	95.90			
Litmus ..	101.80	103.55	103.54	98.93	96.38			
Methyl orange ..	—	123.27	104.21	100.59	98.11			

The number of times the analyst is requested to investigate the purity of refined alkaloids is comparatively small, but the crude alkaloids claim a greater share of his time and attention.

(To be continued).

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY CONVERSAZIONE, JUNE 10TH, 1896.

ALTHOUGH the long expected rain damped everything out-of-doors, there was an exceptionally good attendance at the Soirée of the Royal Society that was held on June 10th.

The exhibits were very numerous and of great interest. Of course, Crookes tubes and Röntgen rays were very much to the front. But real work is now being done in this direction; the mere desire to repeat Dr. Röntgen's experiments is passing away, and some of the first men in science are straining every effort to get more light on this field of research, and probably we shall soon find the disputed points of long or short, transverse or longitudinal waves satisfactorily demonstrated, and thus the way paved for further discoveries.

The very extensive exhibit of Prof. S. P. Thompson, to which we shall refer later on, is a good illustration of this; as was also that of Mr. Herbert Jackson, whose success in the preparation of luminescent screens will greatly help in the study of X rays.

In Room I., The Cambridge Scientific Instrument Company exhibited a Bifilar Pendulum in Action.

Prof. WORTHINGTON, F.R.S., and Mr. R. S. COLE showed a large series of Instantaneous Photographs of Splashes.—These photographs were taken each with an electric spark giving an exposure of less than 3-millionths of a second. The spark could be so timed as to pick out any desired stage of the splash within limits of error not exceeding, as a rule, about 2-thousandths of a second.

Capt. D. WILSON-BARKER, F.R.S.E., exhibited Cloud Photographs taken in different parts of the Ocean World.—Some of these, in particular, were of considerable interest on account of the recent destructive tornado in America.

Prof. W. E. AYRTON, F.R.S., and Mr. T. MATHER exhibited a Small Dynamo for Measuring the Permeability and Hysteresis of Iron.

Mr. J. FRITH showed Different Effects of superimposing a Small Alternating Current on a Direct Current Arc according as Cored Carbons or Solid Carbons are Employed.—This difference was exhibited by the visible motion of the ammeter and voltmeter needles.

In the Council Room, Mr. F. H. WORSLEY-BENISON exhibited a series of Seascape Photographs.—Magnificent specimens of carbon enlargements.

The "Carl Zeiss" Optical Works exhibited their New Portable Binocular Field-glasses and Stereotelescopes.

Dr. JOHN MACINTYRE exhibited a series of Photographs taken by Röntgen Rays that excited very great interest.—(1) Hard tissues. Series of life-size photographs, including bones of head, spine, ribs, extremities, and large joints of body. (2) Soft tissues. Series including neck, tongue, larynx, heart (normal and abnormal), diaphragm, muscles, &c. (3) Animal kingdom. Series of birds, fish, &c. (4) Instantaneous photographs. (Probably got by backing a celluloid film with a fluorescent screen).

The exhibit of Prof. S. P. THOMPSON, F.R.S., to which we have already referred, was very complete, and included—

1. Production by Röntgen's Rays of Electric Dust-shadows.—When Röntgen's rays are allowed to fall upon an electrified sheet of aluminium placed above a plate of ebonite, they carry electric charges to the plate and electrify it. If objects of metal are laid on the ebonite sheet they intercept the Röntgen rays, and the part of the ebonite surface immediately shaded by them does not become electrified. On removing the ebonite plate and

dusting upon it Lichtenberg's powders (mixed sulphur and red lead), the electric shadows become visible.

2. Experiments on Röntgen's Rays.—(a) Cryptoscopic use of luminescent screens (revealing contents of packages, bones of hand, &c.). A large number of new forms of X ray tubes, including one for insertion in mouth, were shown. Also an apparatus of Ebert for producing luminescence by electric oscillations; a stereoscopic X ray photograph of rabbit; and the discharge of electroscope by Röntgen's rays.

Messrs. SIEMENS BROS. and Co. exhibited Electric Discharges in Vacuum.—Facsimile of Dr. Wm. Watson's vacuum tube of 1751. The first apparatus ever constructed for experiments on the electric discharge in a vacuum. The discharge from a Leyden jar passed through 10 inches, and that from a frictional machine through 3 feet, the whole length of the tube. Facsimile of Lord Cavendish's double barometer of 1751. Used by Dr. Wm. Watson in his researches. Facsimile of Dr. Wm. Morgan's shortened barometer of 1785. Dr. Morgan, by long-continued boiling of the mercury in a barometer tube, produced a vacuum of such excellence that no discharge would pass, and equal therefore to that in a Hittorf or Crookes tube of the present day. It is probable that it would have sufficed for the production of Röntgen rays. Apparatus for showing electric discharges at different degrees of exhaustion, from 70 m.m. to 0 m.m. Photographs obtained by means of Röntgen rays, showing relative transparency of different kinds of wood, minerals, and glass. The apparatus shown has been designed by Dr. Eugen Obach.

Mr. F. E. IVES exhibited the Stereoscopic Photo-chromoscope.

Mr. ROBERT L. MOND, M.A., exhibited some of the Apparatus intended for the Davy-Faraday Research Laboratory of the Royal Institution:—

1. Kilogram. automatic balance. (Rueprecht, Vienna).
2. Prism automatic spectroscopy. (Kruss, Hamburg).
3. One-inch spectrometer after Landolt and Brühl. (Hildebrandt, Freiberg).
4. Hüfner photo-spectrometer. (Albrecht, Tübingen).
5. Large polariscope 6-inch Landolt.
6. Small Landolt polariscope. (Schmidt and Haensch).
7. Berthelot platinum bomb. (Golaz, Paris).
8. Glass scale cathetometer. (R. Fuess, Berlin).
9. Petrographical microscope. (R. Fuess, Berlin).
10. Milli-volt meter reading degrees C. for Le Chatelier Thermopile. (Keiser and Schmidt, Berlin).
11. Compensation box of Physikalische Reichsanstalt, Berlin. (Wolff, Berlin).
12. Set of standard resistances. (Wolff).

A more magnificent set of apparatus we doubt if it has ever been the good fortune of any laboratory to possess.

Prof. DEWAR, LL.D., F.R.S., exhibited Portable Apparatus for the production of Liquid Air and Oxygen.

Mr. JOSEPH GOULD gave Demonstrations with his Steel Tuning-bars and Synchronising Sound-generators.

Prof. ROBERTS-AUSTEN, C.B., F.R.S., exhibited Modifications of an Experiment of M. Charles Margot by Professor Roberts-Austen, C.B.—A wire of aluminium is raised, by a current of 30 ampères, to a temperature far above the melting-point of aluminium, but a film of oxide on its surface prevents the wire from breaking. The molten wire through which a current is passing, may then be attracted by a magnet.

Sir DAVID L. SALOMONS, Bart., exhibited a New Form of Spectroscope, with adjustments to vary the width between the lenses.

Mr. T. ANDREWS, F.R.S., showed a number of Photographs taken at high magnifying power of Microscopic Internal Flaws inducing Fracture in Steel Axles, Rails, and Propeller Shafts.

In the Meeting Room, Prof. DEWAR, LL.D., F.R.S., gave a Liquid Air Demonstration, including the following

experiments:—Filtering liquid air; vacuum vessels; boiling at 350 F. degrees below the freezing-point; colour and absorption-spectra; spheroidal state; solid alcohol; frozen soap bubble; distilling mercury and phosphorus; stopping vacuum electric discharge; liquefaction and solidification of gases; fusible metal spring; brittle indiarubber and its expansion by cold; the diamond burning in liquid oxygen; magnetic oxygen; photographic action and phosphorescence; ignition by means of a lens of liquid air; cooling a vessel 380 F. degrees below the freezing-point, until the air of the room condenses on the surface to the liquid state, &c.

PHYSICAL SOCIETY.

Ordinary Meeting, June 12th, 1896.

Captain W. DE W. ABNEY, President, in the Chair.

MR. CAMPBELL read a paper "*On the Measurement of very Large and very Small Alternating Currents.*"

The author advocates the use of air-core transformers, for measuring voltages and currents which are either above or below the range of the instruments available.

If an attempt is made to measure the current in the primary of an air-core transformer by observing the voltage on an open-circuit secondary, it is found that the readings depend on the frequency. In order to overcome this difficulty, the author uses a closed secondary with a very high inductance. In this case the primary current is proportional to the secondary current, which latter may be measured by an ammeter.

The author has also investigated the case of transformers with iron cores, and of which the inductance of the secondary is large. In the case of a ring transformer with a closed magnetic circuit, if the load on the secondary consists solely of a Kelvin 100-ampere balance of very low resistance, the ratio between the primary and secondary currents is practically constant. With an open magnetic circuit transformer, however, this is not found to be so, as the ratio between the primary and secondary currents varies considerably with the frequency.

MR. BLAKESLEY said that the author's arrangement could only be used for measuring the current in the primary. He (Mr. Blakesley) had shown how to measure alternating currents by means of dynamometers, and without the necessity for any special apparatus.

MR. GRIFFITHS exhibited and described his Improved Form of Resistance Box.

This resistance box has many novel features:—

(1). It permits of all the coils being compared with one another, without the use of standard coils and with great ease and rapidity. Hence it is sufficient at any time to compare any one of the coils with a standard to obtain the correction to be applied to all the coils. (2). The bridge wire can be calibrated by means of the box itself. (3). The temperature of the coils can be accurately determined, since they consist of bare platinum-silver wire, wound on mica and immersed in an oil bath, which bath is kept stirred. (4). The resistance of the leads from the box to the object being tested is eliminated, as well as any error due to a change in this resistance with temperature. (5). The coils are arranged according to a binary scale, and the author claims that it is possible to measure resistances up to 105 ohms to within 0.000001 ohm. (6). All the coils, after being adjusted, have been heated to redness and allowed to cool slowly, so that all strain has been removed from the wire. (7). By having a separate pair of blocks for each plug, it is impossible for the insertion of one plug to affect the fit of a neighbouring plug. The plugs themselves are so made that no part of the plug is wider than the top of the hole, and so it is impossible to wear "a shoulder" on the plug.

Prof. A. GRAY said that Mr. Griffiths had discovered and remedied all the weak points of the ordinary form of bridge. Lord Kelvin had ordered the paraffin to be melted off the coils of one of his resistance boxes, and it was found that the resistance of the coils altered considerably, owing, no doubt, to the strain to which the wire had been subjected when embedded in the solid paraffin. Lord Kelvin had made coils without paraffin, and was specially in favour of the use of the binary scale.

Prof. S. P. THOMPSON said he considered the binary scale the weak point of the author's arrangement, since it did not permit of ratios other than 1 to 1 being employed.

MR. CAMPBELL asked what current could be safely passed through the coils.

The author, in his reply, said that he believed it to be a great mistake to employ any ratio for the arms other than 1 to 1.

Prof. S. P. THOMPSON read a communication on "*Röntgen Rays.*"

The author, after describing the various forms of tubes he had made with a view of discovering the best form for the production of Röntgen rays, gave an account of the experiments he had made to try and obtain some indication of polarisation. In this connection a large number of crystals had been tested, but the experiments have all given negative results.

The author exhibited an electroscope with aluminium leaves, and enclosed in a wire gauze screen to protect it from the influence of outside electric changes, by means of which he was able to show the discharge of a positively or negatively electrified body by means of the X rays.

A method of obtaining dust figures by the discharge of an electrified body by the X rays was shown, and some of the results which have been obtained were exhibited.

All attempts to obtain true reflection have failed, although it appears as if most bodies, including air, were capable of giving diffuse reflection.

Dr. SHETTLE, who was announced to give a paper on Röntgen rays, explained that he had just discovered that the effects he had intended to describe were due to red light which had penetrated his dark room.

Prof. DU BOIS said that Galitzine had found that Röntgen rays were polarised by tourmaline, a special form of developer being employed. The behaviour of tourmaline to light waves presents some curious features; for if the wave-length is increased, a point is at length reached where the ordinary and extraordinary rays are equally absorbed. For greater wave-lengths the ordinary conditions are reversed. If the Röntgen rays are not homogeneous, the contradictory results obtained by different observers might be due to the fact that they were working with rays which were differently absorbed by tourmaline.

MR. SWINTON said he had tried the effect of heating the kathode, and had obtained results similar to those which were obtained by the author. Mr. Swinton further said that he had found that the blue luminescence sometimes observed depended on the size of the kathode. With tubes in which the kathode was almost a complete hemisphere, it was impossible to eliminate this blue luminescence.

MR. APPLEYARD suggested the performance of the experiments under the surface of a dielectric.

Prof. GRAY said he had obtained some indication of regular reflection, but nothing definite.

The author, in his reply, said that it had been found that if the Röntgen rays are reflected from a surface of sodium *in vacuo* the amount reflected is a minimum for normal incidence, and increases at oblique incidence. Comparing this behaviour with that of ultra-violet light, it supports the idea that the Röntgen rays consist of transverse vibrations.

The Society then adjourned till June 26th.

CHEMICAL SOCIETY.

Extra Meeting, May 28th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

PROFESSOR P. PHILLIPS BEDSON, M.A., D.Sc., delivered the Lothar Meyer Memorial Lecture.

After relating the more important events in the career of Lothar Meyer, his experimental work on the "Gases of the Blood" was considered, the results of which form the basis of the teaching at the present day. The history of Meyer's independent contribution to the "Periodic Law" was examined, and the development of this system of classification of the elements was traced in Meyer's writings from 1864 to the close of 1869, when he published the paper containing the well known curve of atomic weights and atomic volumes. The investigations of Meyer, undertaken with the object of promoting the systematic arrangement of inorganic chemistry, were noticed. The utilisation of Graham's determination of the rates of transpiration of gases to deduce from them the molecular volumes of gases was next considered, and a description given of the investigations by which it was sought to determine the rates of transpiration of vapours, and thus to arrive at the molecular volumes of vapours. In tracing the history of Meyer's literary work, more especially of the "Modernen Theorien," first published in 1864, of which he was preparing a sixth edition at the time of his death, it was pointed out how great had been Meyer's influence on the promotion and advancement of chemical theory during the past thirty years.

Sir HENRY ROSCOE proposed, and Dr. GLADSTONE seconded, a vote of thanks to Professor Bedson, which was supported by Dr. RUSSELL, and carried unanimously.

Ordinary Meeting, June 4th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

Mr. J. C. Stead was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Walter William Cobb, Hilton House, Atherstone; Arthur Edwin Saville, 33, Richmond Terrace, Darwen; Kotaro Shimomura, Dolemachi, Kioto, Japan; John James Whimster, 12, Rutland Terrace, Stockton-on-Tees; Alfred James Wilcox, The Grammar School, Guisborough, Yorks.

The PRESIDENT announced that the following Address was to be presented to Professor Cannizzaro, a Foreign Member of the Society, on the occasion of his seventieth birthday, in July next.

"ADDRESS TO PROFESSOR CANNIZZARO.

"On behalf of the Council and Fellows of the Chemical Society of London, we, the President and Officers, beg to offer you, Stanislaw Cannizzaro, our most sincere congratulations on the attainment of your seventieth birthday. A society such as ours, having for its object the promotion of chemical science, cannot but acknowledge that your association with us as Foreign Member since 1862, and in 1872 as our Faraday Lecturer, is a source of the greatest satisfaction to all our Fellows, and we desire, in giving expression to this sentiment, to convey to you the wish that your name may for many years continue to add lustre to the roll of our membership.

"At a critical period in the history of our science, when the conceptions of equivalence, atomic weight, atoms, and molecules were ill-defined, and when much confusion existed concerning the fundamental doctrines of chemical theory, you were the first who succeeded in directing the attention of chemists in general to the law which will ever be associated with the name of your illustrious countryman Amadeo Avogadro. Not only did you make

known the importance of this law in its chemical bearings, but with the clearest perception of its far-reaching consequences, you demonstrated in your masterly memoir, 'Sunto di un corso di Filosofia Chimica,' published in 1858, how by its adoption the conflicting views of many of the most eminent chemists of that period could be reconciled and made harmonious. By your advocacy the law of the specific heats of the elements, enunciated by Dulong and Petit in 1819, became more firmly established as an essential principle of chemistry. Our modern methods of determining molecular weight by means of vapour density, and the interpretation of abnormal vapour densities in the light of the theory of dissociation are the direct outcome of your labours on behalf of chemical science. The revised system of the atomic weights of the elements, which has rendered possible their rational classification in accordance with the periodic law of Newlands, Mendeleeff, and Lothar Meyer, and which was necessitated by the acceptance of the hypothesis of Avogadro, has now become universally recognised.

"As one of the founders of the new chemistry, your name will live in the annals of our science as that of a man held in the highest honour and esteem—a name worthy of being joined with those of your great countrymen, Galileo, Torricelli, Volta, and Galvani.

"The congratulations which we now offer you in the name of our Society express the unanimous feeling of the chemists of this country, and not least of ourselves, the officers of the Chemical Society, who are entrusted with the honour of conveying them to you."

The following Address was presented to Lord Kelvin on the occasion of the completion of his fiftieth year as Professor of Natural Philosophy in the University of Glasgow.

"ADDRESS TO THE RIGHT HON. THE LORD KELVIN, D.C.L., LL.D., F.R.S., FROM THE CHEMICAL SOCIETY OF LONDON.

"THE Council of the Chemical Society of London desire to convey to you their sincere congratulations on the occasion of the Jubilee of your Professorship of Natural Philosophy in the University of Glasgow.

"The period during which you have occupied this Chair has been distinguished by the rapid growth of our knowledge of Nature, and the applications of this knowledge to the public good.

"In the past, great names in England and in other countries have been associated with important theoretical advances, and with technical inventions; but it has been given to few, and to none so much as to yourself, to combine a powerful grasp of the most recondite questions in Science with the ability to apply knowledge in an eminently successful manner to the service of mankind.

"With the growing perception of the dependence of one department of Science upon another, we, as Chemists, feel more and more the far-reaching applications of your contributions to Physics, and it is with gratitude and pride in your work that we to-day join with representatives of other Sciences and other nations in offering homage to one whose name will ever occupy a foremost place among the pioneers of Natural Knowledge."

(To be continued).

Physiological Study of Persian Cyclamens.—Alex. Hébert and G. Truffaut.—The methods habitually employed for cultivation on the large scale are not always suitable for the production of flowers. If the distribution of fertilising matters always occasions an abundant production of vegetable matter, this action may fall upon the leaves and not upon the flowers.—*Comptes Rendus*, cxxii., No. 21.

NOTICES OF BOOKS.

Explosives Act, 1875 (38 Vict., c. 17). Twentieth Annual Report of Her Majesty's Inspectors of Explosives; being their Annual Report for the Year 1895. London: Printed for Her Majesty's Stationery Office by Eyre and Spottiswoode. 1896.

THE Inspectors of Explosives, in pursuing their necessary supervision, have not had to chronicle any great calamity, whether due to carelessness or to malice. The outcry raised at the first passing of the Act (1875), that the regulations imposed might fetter competition with alien manufactories, have died away in view of the fact that foreign countries—notably Belgium, France, and Germany—have introduced laws and regulations based to a great extent upon our own, but much more stringent.

The number of deaths from explosions during the year has been ten, a figure above the average during the last ten years, but due not so much to any falling off in the high standard reached in the manufactories, or to negligence on the part of the inspectors as to the increase in the number of factories and in the number of hands employed.

The total number of factories under continuing certificate and license is now 134 (not including "small firework" and "toy firework" factories). This is an increase of four on the previous year. No factories have become extinct.

The four new factories are:—No. 165, for cordite, gun-cotton, and collodion-cotton; No. 166, for Rosslyn smokeless powder No. 1, gun-cotton, and collodion-cotton; and No. 167 and 168, for collodion-cotton.

The following have been added to the list of authorised explosives:—Dahmenite A, electronite Nos 1 and 2, emerald powder, Faversham powder, Pigou's military smokeless powder, Pigou's sporting smokeless powder, roburite No. 3, Rosslyn smokeless powder No. 1, Rosslyn blastite, low tension electric fuzes (No. 5 definition), low tension electric detonator fuzes for ditto.

The limit of quantity of gunpowder, or of ingredients to be made into gunpowder, to be ground under any single pair of mill stones, &c., has been extended to 100 lbs.

Quick-firing ammunition, which was formerly licensed only for direct issue to Her Majesty's land and sea forces, may now be made for export (if water transport only) in the case of one factory on the bank of the Thames. The inspectors have paid 186 visits to the factories, and consider that, as a whole, the factories for explosives in the United Kingdom will compare extremely favourably with any other factories at home or abroad.

The institution of proceedings has been necessary in four cases only.

Some boys broke into a factory near Birmingham, and stole some coloured stars which afterwards exploded, killing one boy. Two cases of illegal manufacture of fireworks have been detected; in one of these a boy was fatally injured.

The list of outrages and attempts at outrage by means of explosives, from 1881 to 1895 inclusive, looks sufficiently gloomy. In those cases where the conviction of the offenders was obtained, the sentences passed were too low. It is a remarkable inconsistency that, whilst there is an outcry against the sale of poisons, no demand is raised for stringent regulation of the common sale of explosives and ammunition, the lawful uses of which are so much more rare and the possible injuries so much greater.

A case against the New Explosives Company, of Stowmarket, for the improper labelling of an explosive, is still pending.

In connection with the question of infernal machines and bombs, it appears that such devices may be safely examined by means of the X rays.

Among Government accidents mention is made of an explosion on board of the War Department powder-barge *Petrel*. The barge ran aground at Hope Point, and the master was drowned. No definite conclusion could be reached as to the cause of the disaster, which is the more unsatisfactory as the vessel was fitted out in exact conformity with the regulation for the carriage of explosives.

On April 22nd an explosion took place at Waltham Abbey in connection with the manufacture of cordite, in which two persons were slightly injured.

An accident occurred during the trial of a Maxim gun, with injury to two persons. The inspectors give a strong caution concerning unexploded charges, or portions of charges, left lying about after gunnery practice or experiments with explosives. This has been the cause of twelve deaths, and of twelve cases of injuries which did not prove fatal. It is recommended that *wooden* tools should be used in searching for or removing any *débris* from such operations.

A serious dynamite explosion took place on Nov. 28th at the Leeuwfontein factory. It is supposed that 50,000 lbs. of dynamite were exploded with widespread damage, but, as the establishment was not working at the time, none of the 800 hands were injured.

The explosions in America have been numerous and serious. On January 15th an explosion ensued at Butte, Montana, resulting in the death of from 75 to 100 persons and injuries to not fewer than 150. It was supposed to be the work of an incendiary, but the perpetrator could not be detected. The explosives were giant powder and gunpowder. On May 21st fourteen persons were killed at Pinola, California, by the spontaneous ignition of impure nitro-glycerin.

At Partenbury, West Virginia, a boat loaded with 250 cans of nitro-glycerin exploded, killing or injuring about 200 persons, and wrecking houses and other property in the neighbourhood.

At Takao, in Formosa, the magazine of one of the forts blew up, and 2000 Chinese soldiers were killed (?).

Two explosions are recorded in India,—one on March 27th in the Kolar gold-field, and the other on April 4th at the Bangalore gold-mine. In each case sixteen persons were killed. The former accident was due to an attempt to steal blasting gelatin, and the latter to the careless handling of detonators.

In Palma, in Majorca, a serious explosion took place on November 21st, killing 92 persons and seriously injuring some others.

A curious accident took place in London on September 21st. A stockbroker, leaving his private office hastily to speak to a client, bumped up against a counter in the outer room. A hissing sound was heard, and his coat was seen to be on fire. It appears that he had some chlorate of potash lozenges loose in his pocket, and at the same time a safety-match box. In bumping against the counter, the lozenges came briskly in contact with the igniting surface of the match-box and occasioned the accident.

Three cases of suicide scarcely deserve particular notice.

Scares and hoaxes have become scarce since two men were fined £48 each for sending bogus bombs to a number of prominent characters.

Explosives intended to produce serious damage, either from motives of private malice or from political feeling, have been numerous. The most serious was that at Tulœ, in Russia, where the artillery barracks were blown up and about 300 officers and soldiers killed. It was supposed to be a Nihilist plot.

Two anarchists were engaged in manufacturing a bomb at Ancona, when it burst and seriously injured them both.

No right-minded person, after duly considering this report, free as it is of anything of an alarmist character, can fail to perceive what a power for evil has been placed in the hands of the criminal classes by the invention of

the "high" explosives, and that their common sale requires to be placed under more stringent regulations.

Book of Tables of Chemico-Organic Compounds: a Work of Reference for Chemists, Apothecaries, Physicians, &c. ("Tabellenbuch der Organisch Chemischen Verbindungen. Ein Hilfs und Nachschlagebuch für Chemiker, Apothiker, Aerzte, &c.") By Dr. Fr. POLLAK. Karlsruhe: Memnich. 1896.

In this most valuable book we find in parallel columns the name of each compound, its formula, the equation showing its origin or preparation, its melting-point, boiling-point, crystalline form and colour, its solubility in water, in alcohol, ether, exceptionally in other organic fluids, and the literature of the substance shown by reference to the abbreviated titles of the principal scientific journals of all countries, and the transactions of the leading scientific societies.

To students, investigators, and manufacturers engaged in the ever-widening field of organic chemistry, this book will prove simply inestimable.

The Old Light and the New. By W. M. ACKROYD, F.I.C. London: Chapman and Hall. Pp. 102.

FROM the outside appearance of this book we expected a mass of information on the discoveries of Dr. Röntgen and others, and we were somewhat disappointed to find the bulk of the space occupied by the theory of colours, &c. The little that there is about the so-called "new light" is meagre, and consists chiefly in the tabulation of some of the more important communications of the various societies in England upon this subject,—valuable indeed in its way, but not exactly what we expected to find. Still we hope it will have a wide distribution, for what little information it does give has the advantage of being clear and concise. Exception must be taken to the position of the X rays in the spectrum diagram on p. 11. Having little or no refrangibility, their place would not be beyond the ultra-violet rays, but they should form a continuation in practically a straight line with the incident white light.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 21, May 25, 1896.

Source and Nature of the Potential directly Utilised in Muscular Work according to the Respiratory Exchanges in a Man in a State of Inanition.—A. CHAUVÉAU.—The author's conclusions are:—According to the evidence supplied by the respiratory exchanges, fat never constitutes the potential directly utilised by the muscles when working in man in a state of abstinence. It is in the form of carbohydrates that this energetic potential is supplied to muscular activity. The work of the muscles tends to exhaust the reserves of glycogen and of glucose when this potential is accumulated. But these reserves, in spite of abstinence, tend to reconstitute themselves in proportion to their consumption.

Immediate Destination of Fatty Foods.—A. CHAUVÉAU, with the collaboration of MM. TISSOT and DE VARIGNY.—As for the immediate destination of alimentary fats, it can be nothing other than the maintenance of the provisions of potential of the organism, whether the reserves of carbohydrates, if these are impoverished

at the moment when digestive absorption has rendered the alimentary fat utilisable, or the reservoirs of adipose tissue where the fatty principles are stored up.

Determination of the Deviation of the X Rays by a Prism.—MM. HURION and IZARN.—The use of two vertical slits situate at some centimetres, the one behind the other, the former of which is illuminated by a source of light of great apparent diameter, furnishes a sort of luminous plane, the upper half of which can be made to pass through a prism.

Refraction of the X Rays.—M. GOUY.—The refraction of the X rays, if it exists, is inferior to two seconds, whence the index cannot differ from unity by more than $1/200,000$. These experiments—with others which the author intends to describe—show the total absence of diffraction.

Action of Gaseous Hydriodic Acid and of Phosphonium Iodide upon Thiophosphonyl Chloride.—A. BESSON.—Hydriodic acid dissolves simply in thiophosphonyl chloride, $PSCl_3$, if we operate in a refrigerating mixture of ice and salt, but a reaction sets in if the temperature of the mixture rises slightly. At the temperature of melting ice the liquid blackens, and hydrochloric acid and hydrogen sulphide are given off. Iodosulphide, P_2Si_2 , is an orange-coloured solid melting at 75° . It is very soluble in carbon disulphide. Ouvrard's phosphorus iodosulphide is yellow, fusible at 106° , and has the composition $P_4S_3I_2$.

Hydration of Pinacoline.—Maurice DELACRE.—This paper is not adapted for useful abstraction.

New Method of Preparing Glyceric Acid.—P. CAZENEUVE.—Glycerin, in presence of soda and silver chloride, gives, if heated, glyceric acid, with the simultaneous production of metallic silver and sodium chloride.

Action of Ethyloxalyl Chloride upon Aromatic Hydrocarbons in presence of Aluminium Chloride.—L. BOUVEAULT.

New Derivatives of Cyanacetic Ethers.—M. GUINCHANT.—These two papers are adapted neither for abridgment nor for insertion in full.

A New Oxidase, or Oxidising Soluble Ferment of Vegetable Origin.—G. BERTRAND.—Laccase is not the only soluble oxidising ferment which exists in plants, but may be regarded as the type of a series of analogous substances.

Zeitschrift für Analytische Chemie.
Vol. xxxiv., Part 6.

Determination of Urea.—B. SCHÖNDORFF, PFLÜGER, and BLEIBTREU.

Detection of Pentoses in Urine.—SALKOWSKI and JASTROWITZ.—The new sugar observed by these authors in human urine is found to be a pentose.

Poisonous Action of Zinciferous Water on Fish.—ED. v. RAUMER (*Forschungs-berichte über Lebensmittel*).—Zinc sulphate, even in very minute quantities, exerts a highly deleterious action upon fishes.

Toxic Action of Different Alcohols on Plants and the Lowest Animals.—M. TSUKANOTO (*Forschungs-berichte über Lebensmittel*).—The toxic action of the saturated alcohols on organisms of different kinds rises with the molecular weight. Isomeric alcohols have not an equally intense action. Allyl alcohol is much more poisonous than the saturated alcohols.

Re-calculation of the Atomic Weights.—J. THOMSEN (*Zeit. Physik. Chemie*).—The author's calculations are based upon the experiments of STAS. The atomic weight of hydrogen appears as 0.9992.

Atomic Weight of Tellurium.—B. BRAUNER.—From the CHEMICAL NEWS.

MEETINGS FOR THE WEEK.

TUESDAY, 23rd.—Photographic, 8.
 WEDNESDAY, 24th.—British Astronomical, 5.
 Society of Arts, 4. (Anniversary).
 Geological, 8.
 THURSDAY, 25th.—Royal Society Club, 6.30. (Anniversary).
 FRIDAY, 26th.—Physical, 5. "Admittance and Impedance," by F. Bedell. "Properties of a Body of Negative Resistance," by S. P. Thompson. "On Bare Wire Resistances," by H. F. Burstall.

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EMISSION OF NEW RADIATIONS BY METALLIC URANIUM.

By HENRI BECQUEREL.

I HAVE shown, some months ago, that the salts of uranium emit radiations the existence of which had not as yet been recognised, and that these radiations possess remarkable properties, some of which may be compared to the properties of the radiation studied by Prof. Röntgen. The radiations of the uranium salts are emitted not only when the substances are exposed to light, but even when they have been kept in darkness, and for more than two months the same fragments of various salts kept secluded from any known exciting radiation have continued to emit new radiations almost without any appreciable decrease. From March 3rd to May 3rd the substances were shut up in an opaque box of cardboard. Since May 3rd they have been placed in a double box of lead, which remained in the dark chamber. A very simple arrangement permitted me to slip a photographic plate below a black paper extended parallel to the bottom of the box, and on it lay the substances in question without these being exposed to any radiation not traversing the lead. Under these conditions the substances studied continue to emit active radiations.

If we expose to the sun, or preferably to the electric arc or to the spark from the discharge of a Leyden jar, a fragment of one of the salts kept in the dark, we communicate to it a slight excitement to the emission of the radiations which we are studying; but this excitement declines in a few hours, and the substance resumes the state of a slow decrease.

I have likewise shown that these radiations are reflected and refracted like light; they decompose the silver salts of a photographic plate and the silver iodide deposited on a Daguerre plate.

They discharge electrified bodies and traverse substances opaque to light, such as cardboard, aluminium, copper, and platinum.

The weakening of these radiations, through the screens which we have just mentioned, is smaller than the weakening of the radiation emanating from the anticathodic wall of a Crookes tube through the same screens.

All the uranium salts which I have studied, whether phosphorescent to light or not, and whether crystalline, melted, or dissolved, have given me comparable results. I have therefore been led to think that the effect was due to the presence of the element uranium in these salts, and that the metal would give effects more intense than its compounds.

The experiment made some weeks ago with commercial powder of uranium which had been kept for a long time in my laboratory confirmed this prevision; the photographic effect is notably stronger than that produced by one of the salts of uranium, and by uranium-potassium sulphate.

Before publishing this result I resolved to wait until our colleague, M. Moissan, whose beautiful researches on uranium are published this day, could place at my disposal some of his recent products. The results have been still more distinct; and the impressions obtained on a photographic plate through black paper with crystalline uranium, cast uranium, and uranium carbide have been much more intense than with the double sulphate used as a check on the same plate.

The same difference has been observed in the phenomenon of the discharge of electrified bodies. Metallic uranium

occasions the dissipation of the charge much more rapidly than do its salts. The following figures relating to the action of a disc of cast uranium, obligingly lent me by M. Moissan, gives an idea of the order of magnitude of this increase.

In a first series of measurement the disc of cast uranium was placed below the gold leaves of a Hurmuzescu electroscope, and very near them. For the initial charges corresponding to 20° deviation of the gold leaves, the speed of approximation expressed in seconds of an angle in one second of time has been as a mean 486. A disc of cardboard, the surface of which was sensibly equal to that of the disc of uranium, was then taken, arranging on it flat fragments of the double sulphate above mentioned, and this disc was then substituted for the disc of uranium. Under these conditions the discharge did not take place regularly, the curve of the deviations of the gold leaves as a function of the time was no longer a right line, and the mean speed of dissipation of charges equal to the foregoing varied from 106.2 to 137.1, according to the disposition and the form of the gold leaves. The ratio of the speeds corresponding to uranium and to the double sulphate has varied therefore between 4.56 and 3.54.

A better disposition consists in placing the substances outside the electroscope above the copper ball of the stem, substituting for the cap of the apparatus a metallic cylinder closed by a flat metal plate perforated with a suitable aperture. We thus obtain discharges very sensibly proportionate to the times and the velocities of loss, for the charges deflecting the gold leaves of 10° have been 78.75 for uranium and 21.53 for the double-uranium potassium sulphate. The relation of the two numbers is 3.65.

Whilst continuing the study of the novel phenomena, I have thought it not uninteresting to signalise the emission produced by the uranium, which is, I believe, the first instance of a metal presenting a phenomenon of the order of invisible phosphorescence.—*Comptes Rendus*, cxxii., p. 1086.

IDENTIFICATION AND SEPARATION OF THE PRINCIPAL ACIDS CONTAINED IN PLANTS.

By L. LINDOT.

THE reactions which enable us to distinguish the vegetable acids are not numerous, and often uncertain in their application; and if we can characterise tartaric acid,—thanks to the insolubility of its potassium salt in the mixture of alcohol and ether,—we are more embarrassed if it is requisite to isolate the other acids, and especially the citric and malic, so frequently present in vegetable tissues.

When studying the compounds of these acids with quinine and cinchonine, I have found that the resulting salts, and especially the acid salts, present differences of solubility in methylic alcohol, such that it is easy to distinguish citric and malic acids and to separate them from vegetable juices.

1. Cold methylic alcohol at 95° Gay-Lussac dissolves only 0.3 per cent of acid quinine citrate; so that if we add quinine to a methylic solution of citric acid, at 2 or 2.5 per cent, this alkaloid is dissolved at first, giving then rise on stirring to a bulky crystalline precipitate of acid citrate, which may extend to 9.3 per cent of the theoretical quantity. An excess of quinine, with reference to the composition of the acid salt, re-dissolves the precipitate, and then ultimately the neutral citrate crystallises; its solubility is greater than that of the acid citrate, and rises to 3.3 per cent.

Under identical conditions the acid quinine malate (solubility in cold methylic alcohol at 95° Gay-Lussac, 8.2 per cent) and the neutral malate (solubility 8.0) remain in solution. The presence of malic acid slightly

interferes with the precipitation of acid quinine citrate, and when in a mixture of the two acids the quantity of malic acid represents 25, 50, 100, or 200 per cent of the quantity of citric acid, the weight of the acid quinine citrate obtained is not more than 99, 97, 94, or 89 per cent of the citrate which would be obtained in a liquid free from malic acid.

Under the same conditions the acid quinine oxalate (solubility 9.2 per cent) and the neutral oxalate (solubility 8.2 per cent) remain equally in solution; but the oxalic acid increases the solubility of quinine citrate in larger proportions than does malic acid.

The precipitate of quinine citrate may be confounded with the quinine acid tartrate (solubility 2.4 per cent) and the acid succinate (solubility 1.2 per cent).

II. Cinchonine dissolved in methylic alcohol precipitates malic acid under conditions identical to those in which quinine precipitates citric acid. However, the solubility of acid cinchonine oxalate in methylic alcohol at 95° Gay-Lussac and in the cold, which is 2.5 per cent, is higher than that of quinine citrate; but the other salts of cinchonine are so soluble that the precipitation above mentioned may be considered as characteristic of malic acid. Acid cinchonine tartrate is, in fact, soluble at 20.6 per cent; the acid nitrate, the acid oxalate, and the acid succinate do not crystallise until their solutions have been brought to the state of syrup. The tartaric, citric, oxalic, and succinic acids, if mixed with malic acid, increase in a striking manner the solubility of cinchonine malate in methylic alcohol; it is thus that citric acid, added to malic acid in the proportions of 20, 50, 100 per cent, hinders the tenth, the half, and even the whole of the oxalic acid from crystallising as a cinchonine salt.

III. To apply the foregoing reactions to the extraction of the acids of a vegetable juice, it must first be evaporated in vacuum, and re-dissolved in methylic alcohol as concentrated as possible. If the juice contains potassium bitartrate and free tartaric acid, it must be treated with alcohol and ether to separate the tartar, and precipitate the tartaric acid in the state of bitartrate by a limited addition of potassa to the same ethero-alcoholic liquor. To eliminate the excess of potassa, we precipitate all the acids by basic lead acetate, and liberate them again with hydrogen sulphide. It is proper to operate in the same manner if the juices contain an excessive quantity of sugars or foreign matters.

The concentrated acids being dissolved in methylic alcohol, we take a known volume of the liquid, which we dilute with methylic alcohol, so that the solution may contain 2.5 per cent of acid, and we add to the liquid increasing quantities of quinine in powder, until after being stirred for some time it sets into a crystalline mass. The quantity of quinine added should not exceed 160 to 170 parts to 100 parts of the citric acid supposed to be present. We must, in fact, avoid adding an excess of quinine, which would dissolve—momentarily at least—the acid citrate, and form neutral citrate, which is more soluble. When the proportion of quinine which must be added has thus been determined, we treat the residue of the liquid with the calculated quantity of quinine. After settling for twenty-four hours we filter, and re-commence the same operation upon the mother-liquor.

If the liquid does not precipitate under these conditions,—that is to say, if it contains no citric acid,—we search for malic acid, by adding in 1 part of the methylic liquid, as concentrated as possible, increasing quantities of cinchonine, the maximum dose of which may be fixed at 140 to 150 per cent of the estimated quantity of malic acid.

If the two acids are simultaneously present, when the liquid is no longer precipitated by quinine we add cinchonine, the action of which is not interfered with by the excess of quinine.

It is easy to recover the corresponding acids from the salts of quinine and cinchonine obtained. It is sufficient to add to the aqueous solution of these salts ammonia, to filter off the alkaloids, to precipitate the liquid with

basic lead acetate, and then decompose the precipitate with hydrogen sulphide. Or we may render both the acid and the base insoluble by means of baryta, exhaust the dried precipitate with alcohol, and decompose the barium salt with sulphuric acid.

By these methods I have been able to extract the citric acid contained in lemons and gooseberries, and extract the malic acid contained in cherries.—*Comptes Rendus*, cxxii., p. 1185.

PREPARATION AND PROPERTIES OF URANIUM.

By HENRI MOISSAN.

In a paper published on February 20th, 1893, we have established that uranium oxide, hitherto regarded as not reducible by carbon, can yield metallic uranium in presence of this substance at the high temperature of my electric furnace. We have since demonstrated the existence of a definite crystalline compound of uranium and carbon, C_3U_2 .

We shall now give a more complete study of this metal.

It is known that metallic uranium was first prepared by Peligot by reducing uranium chloride with potassium in a platinum crucible. By this procedure we obtain a grey powder, in the midst of which are found some small metallic globules.

Different chemists have slightly modified this operation, and in 1886 Zimmermann resumed the study of uranium, and obtained the metal by reducing uranium chloride with sodium. The isolated metallic globules in this preparation were few in number. Their fusion was due to the intense heat developed by the action of the alkaline metal upon the chloride.

We have repeated all these experiments. If we operate in a platinum crucible, the uranium is always soiled with this metal. In Zimmermann's preparation the uranium always contains 2 per cent of iron and a small quantity of sodium.

Moreover, whatever is the method employed, all these uranums in powder contain nitrogen and often oxygen. As we shall demonstrate below, metallic uranium has a strong affinity for gaseous nitrogen, hitherto unknown.

We thought that this action of the alkaline metals might be more advantageously employed by means of a double compound of sodium and uranium.

Preparation of the Double Uranium and Sodium Chloride, $UCl_4 \cdot 2NaCl$.—When we pass a current of vapour of uranium chloride over sodium chloride we obtain a double chloride, which on cooling congeals to a crystalline mass of an apple-green colour, melting at 390°, fusible about 390°, soluble in cold water, and dissociated by alcohol.

This preparation is very easily made in a tube of Bohemian glass, forming at one end uranium chloride by the action of chlorine upon uranium carbide, and causing this chloride to pass over fragments of sodium chloride placed at the other end and heated to dull redness. The solid alkaline chloride begins to be coloured, seizing all the vapour of uranium chloride, and then the mass melts rapidly.

We know that uranium chloride, UCl_4 , is greedy of moisture, fumes in the air, and is not easily manageable. On the contrary, the crystalline double chloride is much less hygroscopic and more stable. If fused, it yields a very stable liquid, which does not apparently give off vapours.

Reduction of this Double Chloride by Alkaline Metals.—The reduction has been effected in a very thick iron cylinder, closed with a screw stopper. It is charged with alternate layers of 300 grms. double chloride and 100 grms. sodium recently cut.

The apparatus being closed, it is placed in a very brisk wood fire, when it is heated for twenty-five minutes. The heat disengaged by the reaction is so intense as to raise the block of iron to a cherry-red heat in a few instants. When cold, the cylinder is opened, and the powdery contents treated at first with alcohol at 96° to remove the excess of sodium, then rapidly washed with water which has been boiled and allowed to cool, then exhausted with alcohol and lastly with ether.

Preparation of Uranium in the Electric Furnace.—We have indicated in a former paper on uranium carbide how the industrial uranium carbide must be purified. The uranium having been brought to the state of green oxide (U_3O_8), is intimately mixed with sugar charcoal in fine powder in the following proportions:—

Uranium oxide	500 grms.
Sugar charcoal	40 "

About 500 grms. of this mixture are placed in a coke crucible and submitted in the electric furnace for seven to eight minutes to a current of 800 ampères and 45 volts. We thus obtain a fused ingot of about 350 grms. The metal thus prepared, if the heating has been well conducted, contains very little carbon, and sometimes even not a trace. On the contrary, we may find in it a small quantity of oxide, which then furnishes a "burnt metal," the physical properties of which are notably modified. If the duration of the heat is too long, the metal is readily carbided, and we obtain a cast metal and then a crystallised carbide, C_3U_2 . To avoid the action of nitrogen, it is better to make these experiments in a tube of coke closed at one end, and adopting the arrangement above indicated.

Refining Uranium at the Forge.—When we prepare by the above procedure an uranium containing from 0.1 to 0.5 of carbon, we may refine the exterior of the fragments by heating them for some hours in a crucible lined with green uranium oxide. To realise this experiment we must place the crucible containing the uranium oxide and the metal in the middle of another crucible filled with titaniferous carbon finely pulverised. The neglect of this precaution might produce a yellow metal coated with nitride.

Preparation of Metallic Uranium by Electrolysis.—The double uranium chloride above described is electrolysed with the greatest ease. It yields at the negative pole a sponge of uranium containing frequently small crystals of this metal. To have regular working it is sufficient to have at the terminals a difference of potential of 8 to 10 volts. We have generally used a current of the density of 50 ampères. The bath is kept in fusion by the thermic action of the current itself.

The electrolysis is effected by means of electrodes of pure charcoal, and the chloride is placed in a cylindrical vessel of porcelain. This vessel is closed by means of a plate of porcelain, giving passage to the two electrodes and to a glass tube bent at a right angle. This tube enables us to introduce above the melted salt a current of hydrogen very dry and very free from nitrogen.

After complete cooling, the contents of the crucible are taken up with ice-water, and washed rapidly with alcohol; for uranium, if finely divided, decomposes water at the ordinary temperature.

This uranium is crystalline, and certain parts near the electrode appear even in crystals measuring 1 m.m. on the sides.

If we employ an iron electrode, we obtain alloys of iron and uranium of a silvery white, which may be easily filed and which have a very fine grain.

Physical Properties.—When uranium is very pure its colour is absolutely white, less bluish than that of iron, though it takes a similar polish. If the metal has a yellow tint, we may always suspect the presence of nitrogen. To its specific gravity we shall return below.

Pure uranium may be easily filed: it does not scratch

glass. It may be slightly carbided if heated in a crucible lined with carbon, and may be tempered.

Uranium is not magnetic when quite free from iron.

In the electric furnace uranium is much more volatile than iron.

Chemical Properties.—Uranium in fine powder, as prepared by electrolysis, takes fire in fluorine, burns brilliantly, and forms a volatile fluoride of a green colour. Chlorine attacks it at the temperature of 180°, and bromine at 210°, both with incandescence. The same reaction is produced in the vapour of iodine about 260° with formation of uranium iodide. All these reactions are complete. The metal obtained by Zimmermann was not attacked by the vapour of iodine, and in a current of chlorine it underwent a limited reaction, leaving in the boat an abundant residue.

Hydrochloric acid gas attacks it with incandescence at a dull red heat, yielding a stable chloride which produces a green solution in water. Hydriodic acid attacks it near a red heat.

Uranium in fine powder burns in pure oxygen at 170° and upwards, producing a very dark green oxide. Sulphur reacts about 500°, furnishing a black sulphide which is slowly attacked by hydrochloric acid, yielding hydrogen sulphide. With selenium it combines with incandescence.

As we have remarked above, uranium combines with nitrogen with the greatest ease. Fragments of the metal heated to 1000° in a current of nitrogen became covered with a yellow layer of nitride. Uranium in powder reacts with gaseous ammonia above dull redness, but without incandescence, producing an escape of hydrogen and leaving a black crystalline powder, which we are now examining.

Pure uranium in very fine powder decomposes water slowly at ordinary temperatures and more rapidly at 100°. This property approaches it to iron, since, according to our colleagues Troost and Hautefeuille, reduced iron decomposes water at its boiling point.

Melted uranium in contact with water is covered with a layer of oxide; this action is strikingly accelerated by the presence of carbonic acid.

Analysis.—In all these researches the uranium has been separated and determined in the form of U_3O_8 , and the carbon weighed as carbon dioxide.

Double uranium-sodium chloride yielded on analysis the following figures:—

	1.	2.	3.	Theory.
Uranium ..	47.9	47.7	48.2	48.08
Sodium ..	—	—	10.10	9.21
Chlorine ..	42.3	42.4	42.01	42.68

Metallic uranium prepared by sodium gave:—

Uranium	99.40	99.28
---------------	-------	-------

The specimen always contained traces of the alkaline metal. The metal prepared in the electric furnace contained:—

	1.	2.	3.	4.
Uranium ..	99.121	99.106	98.021	99.520
Carbon ..	0.168	0.601	1.356	0.005
Slag	0.187	0.204	0.303	0.421

Uranium obtained by electrolysis:—

	1.	2.
Uranium	99.27	94.48
Insoluble in nitric acid ..	0.52	0.27

Conclusions.—Metallic uranium may be easily obtained either by decomposing the double uranium and sodium fluoride with sodium, or by the electrolysis of the same compound, or preferably by reducing uranium oxide with carbon in the electric furnace. These three methods yield good results, and for these researches we have had occasion to prepare more than 15 kilos. of metallic uranium.

Uranium may be obtained crystallised; the pure metal has properties approaching those of iron. It can be filed,

carbided, tempered, and oxidised in the same manner. Its tendency to combine with oxygen is greater than that of iron; in fine powder it decomposes water slowly in the cold; its reaction with the hydracids is also more energetic than that of iron. It has a most powerful affinity for nitrogen, and without special precautions the product obtained always contains a certain quantity of this element.

This metal when quite free from iron has no action upon the magnetic needle, and in the electric furnace it is much more volatile than iron.—*Comptes Rendus*, cxxii., p. 1088.

ACIDIMETRIC ESTIMATION OF VEGETABLE ALKALOIDS. A STUDY OF INDICATORS.*

By LYMAN F. KEBLER.

(Concluded from p. 288).

THE next step was to investigate the adaptability of the above process to crude morphine and crude cocaine. The results are as follows:—

Indicators.	Crude morphine.		Crude cocaine.
	LaWall.	Kebler.	Kebler.
Brazil wood ..	99'23	98'47	95'90
Cochineal ..	100'14	99'53	97'11
Hæmatoxylin ..	99'08	97'59	95'74
Litmus ..	99'50	98'93	96'82
Methyl orange	102'10	100'02	100'14

With the same crude morphine the ash method yielded 97'59 per cent, the lime-water method 98'22 per cent, and the absolute alcohol method 98'33 per cent of pure morphine.

A complete analysis was made of the crude cocaine to ascertain how nearly the titrations corresponded with the gravimetric process of Dr. Squibb (*Ephemeris*, iii., 1171).

	Per cent.
Moisture	0'405
Cocaine nearly pure..	97'300
Material soluble in ether ..	0'100
Material insoluble in ether ..	1'810
Loss	0'385
Total	100'000

Notwithstanding the fact that crude alkaloids claim considerable attention on the part of the analyst, yet only a few are found already extracted on the market. It generally happens that the operator is requested not only

to determine the amount of pure alkaloids, but also to extract them from their natural sources. For this purpose the writer employed a modification of Keller's process. The method is as follows:—Place 10 grms. of the dry drug into a 250 c.c. flask; add 25 grms. of chloroform, 75 grms. of ether, stopper the flask securely, agitate well for several minutes, add 10 grms. of 10 per cent ammonia water, then agitate frequently and during one hour. On adding 5 grms. more of 10 per cent ammonia water and shaking well, the suspended powder agglutinates into a lump, the liquid becomes clear after standing a few minutes, and can be poured off almost completely.

1. When the mixture has completely separated, pour off 50 grms. into a beaker, evaporate the solvent on a water-bath, add 10 c.c. of ether, and evaporate again. Dissolve the varnish-like residue in 15 c.c. of alcohol, with heat, add water to slight permanent turbidity, the requisite quantity of indicator, and an excess of the acid solution; re-titrate with the centinormal alkaline solution.

2. When the mixture has completely separated pour 50 grms. into a separatory funnel, treat at once with 20 c.c. of acidulated water. After thorough agitation and complete separation, remove the aqueous solution into a second separatory funnel. Repeat the above operation twice more successively with 15 c.c. of slightly acidulated water. The acidulated water in the second separatory funnel is rendered alkaline with ammonia water, the alkaloid removed successively with 20 c.c., 15 c.c., and 15 c.c. of a mixture of three parts (by volume) of chloroform and one part of ether. Collect the chloroform-ether mixture in a tared beaker, and distil off the solvent. The varnish-like residue is twice treated with 8 c.c. of ether, evaporated on a water-bath, and dried to constant weight on the water-bath. The varnish-like residue is next dissolved in 15 c.c. of alcohol, and treated as in 1 above.

Nux vomica and ipecac root were treated according to processes 1 and 2; belladonna leaves according to process 2. The results are given below.

According to the well-established method of Messrs. Dunstan (1883, *Pharm. J. Trans.* [3], xiii., 665) and Short, the nux vomica examined contained 2'89 per cent of crude alkaloid. On carefully titrating this crude product with a volumetric acid solution, 2'12 per cent of pure alkaloid was indicated. Cochineal was used as an indicator. These figures show that this method produces an alkaloid residue containing a smaller percentage of pure alkaloid than that obtained by Keller's process.

From the results embodied in this paper it can safely be concluded that methyl orange cannot be numbered with the indicators suitable for titrating alkaloids. With centinormal, fifth decinormal, and other solutions of various strengths, it fails to give satisfactory results.

* Read at the Springfield Meeting. From the *Journal of the American Chemical Society*, vol. xvii., No. 10, October, 1895.

	Per cent of alkaloids in nux vomica by process 1.		Per cent of alkaloids in nux vomica by process 2. Gravimetrically.		Per cent of alkaloids in nux vomica by process 2. Volumetrically.		Per cent of alkaloid in ipecac root by process 1.	
	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.
Brazil wood..	2'04	2'58	2'94	3'00	2'37	2'37	2'46	2'54
Cochineal ..	2'64	2'69	2'86	3'10	2'42	2'39	2'59	2'49
Hæmatoxylin ..	2'18	2'24	2'88	3'11	2'23	2'27	2'48	2'54
Litmus ..	2'38	2'34	2'93	3'05	2'55	2'37	2'55	2'57
Methyl orange	3'02	3'64	2'93	3'02	2'65	2'61	2'95	3'30
	Per cent of alkaloid in ipecac root by process 2. Gravimetrically.		Per cent of alkaloid in ipecac root by process 2. Volumetrically.		Per cent of alkaloids in belladonna leaves by process 2. Gravimetrically.		Per cent of alkaloids in belladonna leaves by process 2. Volumetrically.	
	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.
Brazil wood..	2'58	2'60	2'36	2'35	0'26	0'20	0'19	0'15
Cochineal ..	2'63	2'68	2'52	2'33	0'28	0'20	0'24	0'14
Hæmatoxylin ..	2'58	2'68	2'35	2'33	0'27	0'22	0'21	0'13
Litmus ..	2'62	2'60	2'40	2'25	0'24	0'18	0'20	0'15
Methyl orange	2'66	2'63	2'89	2'61	0'25	0'20	0'23	0'20

Notwithstanding the sensitiveness claimed for it, the writer believes that its days, as an ideal indicator, are numbered. Even Professor Lunge, the staunch advocate of methyl orange, has admitted that a properly prepared solution of litmus is quite superior to this indicator, in inorganic estimations.

A solution of litmus prepared according to the directions herein employed is quite unsatisfactory for delicate titrations. The method proposed by Reinitzer promises to be better suited.

Of the indicators thus far considered, hæmatoxylin, Brazil wood, and cochineal give very promising results. Hæmatoxylin justly claims first place, and Brazil wood the second. Other indicators will be considered in due time.

As stated above, the prime object of this investigation is to ascertain what indicators are best adapted to the titration of alkaloids; but in order to determine how reliable the results were, gravimetric determinations necessarily formed a part of the work.

When it is remembered that not only do analytical methods contain inherent limitations, but also that each operator possesses a positive or a negative equation of error, the reader will undoubtedly concur with the writer that the results are very satisfactory. Attention must again be called to the fact that the work was conducted under precisely the same conditions.

As would naturally be expected, the amount of alkaloid obtained by process 2 is smaller than that secured by process 1. A small per cent of the alkaloid may be lost during the process of extraction. The small amount of colouring-matter possibly vitiates the results, or perhaps some non-alkaloidal substance increases the yield in process 1.

From the hundreds of assays made by the author, he feels justified in stating that all of the gravimetric processes yield products containing considerable non-alkaloidal matter, and hopes that the day is not far distant when all gravimetric results will at least be supplemented by volumetric methods, if not displaced by them.

The more Valuable Literature on Indicators during the last Two Decades.

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PHOTOMETRIC METHOD

FOR THE

QUANTITATIVE DETERMINATION OF LIME AND SULPHURIC ACID.

By J. I. D. HINDS.

(Concluded from p. 287).

For Calcium Carbonate.

IN the investigation of lime I used a solution of calcium chloride whose strength corresponded exactly to 0.001 gm. of CaCO_3 to the c.c. Ten c.c. of this solution were taken and diluted with 20 c.c. water; then enough solid ammonium oxalate was added to precipitate the whole of the calcium. The solution was then poured into the photometric cylinder and the depth measured as in the case of the sulphuric acid. Portions of 10 or 20 c.c. of water were successively added and the depth observed after each addition. The results are given in the following table. In column 1 is the number of the solution; col. 2 shows the per cent of CaCO_3 ; cols. 3, 4, 5, 6, and 7 contain the measured depths of the liquid at which the flame became invisible; col. 8 contains the means of these depths; and col. 9 the product of these means by the per cents in col. 2, represented as before by xy . The three determinations in the fifth series were made simply as a check. Many other independent determinations were made in order to ascertain whether there was a change of opacity, and whether the precipitation would be different in the weaker solutions. No material difference was found.

	P.c. y.	C.m.	C.m.	C.m.	C.m.	C.m.	x .	xy .
1.	0.0333	2.1	2.3	2.3	2.3		2.250	0.0750
2.	0.0250	2.8	2.9	2.9	2.9		2.875	0.0718
3.	0.0200	3.5	3.6	3.5	3.5		3.525	0.0705
4.	0.0167	4.1	4.2	4.1	4.1	4.2	4.14	0.0691
5.	0.0143	4.7	4.8	4.7	4.7		4.725	0.0676
6.	0.0125	5.3	5.5	5.3	5.3		5.35	0.0669
7.	0.0111	6.0	6.1	5.9	6.0		6.0	0.0666
8.	0.0100	6.6	6.8	6.6	6.7		6.675	0.0668
9.	0.0091	7.3	7.4	7.3	7.4	7.4	7.36	0.0670
10.	0.0083	8.0	8.0	8.0	8.1		8.03	0.0666
11.	0.0077	8.8	8.6	8.6	8.8		8.7	0.0670
12.	0.0071	9.5	9.3	9.3	9.5		9.4	0.0667
13.	0.0067	10.2	9.9	9.9	10.1	9.9	10.0	0.0670

Examining the various values of xy , we find that they are not constant. They diminish rapidly at first, then more slowly. The equation is, therefore, not so simple as in the case of the sulphuric acid. It appears, however, to be a hyperbola, and we may assume that its equation has the form—

$$xy + by = a,$$

in which b and a are constants whose values are to be determined. Substituting the values of x and y from the above table we obtain thirteen observation equations. The values of a and b are then found according to the method of least squares by forming and solving the two sets of normal equations. The first set will be the same as the observation equations; the second set is obtained

by multiplying each equation by its coefficient of b . These equations are as follows:—

$$\begin{array}{ll} 0.0750 + 0.0333 b = a & 0.002500 + 0.001111 b = 0.0333 a \\ 0.0718 + 0.0250 b = a & 0.001795 + 0.000625 b = 0.0250 a \\ 0.0705 + 0.0200 b = a & 0.001410 + 0.000400 b = 0.0200 a \\ 0.0691 + 0.0167 b = a & 0.001151 + 0.000271 b = 0.0167 a \\ 0.0676 + 0.0143 b = a & 0.000967 + 0.000204 b = 0.0143 a \\ 0.0669 + 0.0125 b = a & 0.000836 + 0.000156 b = 0.0125 a \\ 0.0666 + 0.0111 b = a & 0.000740 + 0.000123 b = 0.0111 a \\ 0.0668 + 0.0100 b = a & 0.000668 + 0.000100 b = 0.0100 a \\ 0.0670 + 0.0091 b = a & 0.000610 + 0.000083 b = 0.0091 a \\ 0.0666 + 0.0083 b = b & 0.000553 + 0.000069 b = 0.0083 a \\ 0.0670 + 0.0077 b = a & 0.000516 + 0.000059 b = 0.0077 a \\ 0.0667 + 0.0071 b = a & 0.000474 + 0.000050 b = 0.0071 a \\ 0.0670 + 0.0067 b = a & 0.000449 + 0.000045 b = 0.0067 a \end{array}$$

Adding the equations together we have—

$$0.8886 + 0.1818 b = 13a \quad 0.012668 + 0.003304 b = 0.1818 a$$

Dividing by the coefficient of a and eliminating, we have—

$$a = 0.0642 \quad b = -0.3$$

The required equation is therefore—

$$xy - 0.3b = 0.0642,$$

or solving for y —

$$y = \frac{0.0642}{x - 0.3}$$

This is the equation of an hyperbola referred to one of its asymptotes as the axis of x , and to an axis of y three-tenths of a centimetre to the left of the other asymptote. The curve is shown by the lax upper line in the diagram. The dotted line is the asymptote.

As an example, let us suppose that the observed depth is 4.7 c.m. Subtract 0.3 and divide 0.0642 by the remainder. The quotient, 0.0146, is the per cent of CaCO_3 . Dividing this by 1000, we have 14.6 parts to the 100,000.

For the per cent of CaO the equation is—

$$y = \frac{0.0360}{x - 0.3}$$

To determine the probable error, we may, as before, compare a set of observations with the numbers computed from the equation as follows:—

x .	Strength used.	Strength computed.	v .	v^2 .
2.9	0.0250	0.0247	0.0003	0.00000009
3.5	0.0200	0.0201	0.0001	0.00000001
4.1	0.0167	0.0170	0.0003	0.00000009
4.7	0.0143	0.0146	0.0003	0.00000009
5.35	0.0125	0.0127	0.0002	0.00000004
6.0	0.0111	0.0112	0.0001	0.00000001
6.7	0.0100	0.0100	0.0000	0.00000000
7.4	0.0091	0.0091	0.0000	0.00000000
8.0	0.0083	0.0085	0.0002	0.00000004
8.7	0.0077	0.0077	0.0000	0.00000000
9.4	0.0071	0.0071	0.0000	0.00000000
10.0	0.0067	0.0066	0.0001	0.00000001

$$\text{Sum, } \Sigma v^2 \quad \dots \quad 0.00000038$$

Using the same value for error as before, in which in this case n , the number of observations is 12, and q , the number of constants in the equation, is 2, we have—

$$r = 0.6745 \sqrt{\frac{0.00000038}{12-2}} = 0.00013 \text{ p.c.}$$

That, is the probable difference between an observed and computed strength of a solution is 0.00013 per cent, or 1.3 parts in a million.

Sources of Error.

The principal sources of error in the method are two. In the first place a light of constant intensity should be

used. It makes but little difference what the light is, so it is the same as that with which the constant is determined. I employed the flame of an ordinary candle as the most convenient. A brighter and steadier light would give better results. Any change of light would of course change the constants in the equations.

The second source of error is the personal equation. Each individual can determine this for himself. The error dependent upon the eye can be almost eliminated by using it in the usual way, that is with or without glasses.

Each individual can obtain the constants for himself by making a few determinations with solutions of known strength. The best strength to use is that between 0.01 and 0.02 per cent. Great care must be taken in measuring. If 10 c.m. of a decinormal solution are taken, a difference of one drop in the measurement may make an error ten times as great as that involved in the method. So also I found that a difference of 5° in temperature was sufficient to sensibly affect the determinations.

Practical Application.

I have so far used the method and tested it only in sanitary water analysis and in the analysis of urine. To the water analyst it will be of great value. It gives the lime and sulphuric acid with almost the accuracy of the gravimetric method. It is more accurate than the soap test and is but slightly affected by the presence of magnesium salts. Of course the water must be clear.

For determining the sulphuric acid in urine I found it quite satisfactory. The urine has to be diluted with nine volumes of water, and then the colour does not sensibly affect the determination.

I see no reason why this method may not be satisfactorily used for approximate determinations with all fine white precipitates. It is not applicable to precipitates which settle rapidly or gather quickly into flakes. Whether coloured precipitates may be determined in this way is still to be investigated.

I desire to acknowledge obligations to Professor A. H. Buchanan for assistance in determining the equations and probable errors.

Chemical Laboratory, Cumberland University,
Lebanon, Tenn., U.S.A.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING MAY 31ST, 1896.

By WILLIAM CROOKES, F.R.S.,
and
PROFESSOR DEWAR, F.R.S.

To MAJOR-GENERAL A. DE COURCY SCOTT, R.E.,
Water Examiner, Metropolis Water Act, 1871.

London, June 9th, 1896.

SIR,—We submit herewith, at the request of the Directors, the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from May 1st to May 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to

oxidise the organic matter in all the samples submitted to analysis.

Of the 175 samples examined all were found to be clear, bright, and well filtered.

The prolonged drought in the Thames Valley has been even more marked during this month than in several of the preceding months of this year; the total rainfall at Oxford for May was 0.2 inch, of which 0.15 inch fell on the 21st; the 30 years' average being 1.83 inches, there is a deficiency of 1.63 inches, or 89 per cent, for the month. The total deficiency for this year is now 4.69 inches, or more than 50 per cent on the 30 years' average.

Our bacteriological examinations gave the following results:—

	Colonies per c.c.
Thames water, unfiltered	1301
Thames water, from the clear water wells of the five Thames-derived supplies.. highest	34
Ditto ditto lowest	12
Ditto ditto .. (12 samples) mean	21
New River water, unfiltered	950
New River water, from the Company's clear water well	25
River Lea water, unfiltered	1216
River Lea water from the East London Com- pany's clear water well	73

These results show that the London water supply is thoroughly and efficiently filtered, and that the condition of the rivers leaves little to be desired.

The chemical composition of the waters shows that the organic carbon and organic nitrogen are exceptionally low.

The following table gives the difference in chemical composition of the five Thames-derived supplies for the months of May, 1895 and 1896:—

	Common Salt. Per gall. Means.	Nitric Acid. Per gall. Means.	Oxygen. Hardness. Degrees. Means.	Organic reqd. Per gall. Means.	Organic Carbon. Per gall. Means.	Organic Carbon. Per gall. Max.	Colour. Br'n:Blue. Means.
May,							
1895. 1.994	0.908	14.41	0.045	0.128	0.206	13.5:20	
1896. 2.055	0.871	15.89	0.033	0.064	0.078	10.6:20	

We are, Sir,

Your obedient Servants,

WILLIAM CROOKES.
JAMES DEWAR.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 4th, 1896.

Mr. A. G. VERNON HARCOURT, President, in the Chair.

(Concluded from p. 291).

OF the following papers that marked * were read:—

*73. "On Magnetic Rotatory Power, especially of Aromatic Compounds." By W. H. PERKIN, LL.D., Ph.D., F.R.S.

This paper gives an account of the apparatus used in measuring molecular rotations, at temperatures up to about 100°, also particulars concerning the determinations of boiling-points and densities, with a description of the apparatus used for the latter purpose when it is necessary to determine them up to temperatures of about 100°, and also for substances which are solid at ordinary temperatures.

The results obtained on determining the rotation of mixtures of compounds where the specific rotations are

wide apart, and of those where they are nearly identical, are then considered, and it is seen that, under the first circumstances, rotations are obtained which are not the mean of those of the constituents of the mixture, but lower, whilst in the latter case they are the mean of the two. The most striking differences obtained are those with mixtures of ethylic nitrate and carbon disulphide.

The next subject is that of the influence of varying temperatures on the rotations. The results obtained show that all substances yet examined, water excepted, fall slightly in rotation as the temperature rises. The amount varies with different classes of substances.

This difference in the change of rotation is called the *temperature-difference*, and the results are analogous to those obtained when the refractive power of compounds is determined under similar circumstances. The rotation of water, which does not fall with the density, as with other substances, evidently increases slightly with rise of temperature. This is thought to be due to the breaking down of molecular complexes.

The next section refers to the magnetic rotations of aromatic compounds, and comprises ethereal salts, mixed oxides containing phenyl and alcohol radicles, &c., phenylic salts of the fatty acids, hydrocarbons, phenols, alcohols, aldehyds, ketones, nitriles, nitro-compounds, haloid and sulphur compounds, amines, unsaturated compounds, &c.

From the results obtained with these different classes of substances it is seen that there is a great difference between the rotations of aromatic and fatty compounds, the effect of the nuclei contained in them greatly influencing the rotation.

It is found that in many cases the substances behave like double molecules, the part containing the fatty groups acting like a fatty compound, whilst that containing the nucleus acts in a different manner. This occurs more especially where a carbonyl group exists between the nucleus and the fatty groups, in which position it acts like a screen between them. Some other groups also behave in this manner more or less effectively.

The nucleus is also influenced by the groups and haloids it is associated with; thus with nitroxyl and fluorine its influence is greatly reduced, and it is also reduced, but not to nearly so large an extent, by carbonyl, and also by chlorine; all being strongly electro-negative elements and groups. On the other hand, it is much increased by association with hydrocarbon groups, especially when unsaturated, and greatly by the electro-positive amidogen group and its methylated and phenylated derivatives.

With reference to the effect produced by the nitroxyl group, it is thought that possibly the oxygen in this compound may be in a para-magnetic condition, as oxygen is when in the free state, and especially when in the liquid condition. If so, this would account for the very low rotation of this compound, as it would have a negative rotation. If this be so, the inference is that fluorine is also paramagnetic; the very low rotation of sulphuric acid and phosphoric acid, containing sulphur and phosphorus, which have very large rotations, would also become easily explainable if the oxygen they contained were paramagnetic.

The variation in the influence of the nucleus on the rotation was found to be very considerable, even in hydrocarbons, the influence increasing as two or more nuclei become more and more nearly associated, and at last come into direct union, as in diphenyl. This, however, does not appear to arise from mass action.

The effect produced by the association of the benzene nucleus with the unsaturated group $-\text{CH}=\text{CH}-$ is also found to be very remarkable, and especially so when two are united with it, one on each side, as in stilbene, the result being nearly ten times as great as when this group is in the fatty compounds.

From the results obtained it is evident that no fixed value can be found for phenyl in hydrocarbons or other

aromatic compounds, nor yet for naphthyl; at the same time the rotations do not give any constant values for the groups which are directly associated with the nucleus. Thus, the influence of NH_2 entering a paraffin raises its rotation by 0.971, but in benzene 4.792, and in naphthalene, for the α -position, 12.353. From these results it is seen that it would be absurd to assume that this group has these widely different values, or that the carbon and hydrogen in the nucleus has changed so as to share in this great increase. It is noticed also that these great changes take place in cyclic compounds only.

The fact that in naphthalene both nuclei are apparently equally affected by the introduction of nitroxyl or amidogen, although the displacement taking place is one only, suggests that there is a kind of inductive influence going on in these compounds from one carbon to the other; especially as the effect of some of the groups approximates to the ordinary influences found in the fatty series, multiplied by the number of carbon atoms in the nuclei, the amount being sometimes rather lower and sometimes rather higher. Taking aniline as an example, the increase in rotation for the amidogen group in the nucleus, although not six times as great as the ordinary influence of amidogen in the fatty series, is yet nearly five times that amount. In the naphthalene series it is rather more than ten times as great in the β -compound, whilst in the corresponding α -compound it is twelve times as great.

Diphenylamine affords an interesting example in this connection, the two separate molecules being united by NH . The influence it exerts appears to be not much less than twice that of this group in aniline, both nuclei being evidently equally influenced.

From these results it appears that these great changes in rotation must be chiefly due to physical influences, and that only a part of their effect can be attributed to the rotatory power of the atoms contained in the molecule.

The high refractive power of these compounds apparently must also be due to the physical nature of the molecules, and not simply to their chemical composition.

It is considered doubtful whether only one kind of physical condition would account for all that takes place in such compounds containing the benzene nucleus, as besides smallness and largeness of rotation, there are other differences to be accounted for.

The physical conditions due to the arrangement of the atoms in the molecules of saturated carbon compounds, being more simple than those connected with the unsaturated or cycloid compounds, have only a comparatively small influence on the rotation, yet each series of these compounds has an initial influence of its own, dependent on the series group, or special molecule, such as COOH , CO , COH , OH , &c., and for calculating the rotations of members of these different series, a set of *series constants* had to be prepared. These variations cannot evidently be due to change in the rotatory power of the elements, but must be caused by the physical conditions induced by molecular arrangement.

On considering the refractive power of saturated compounds, it is found that similar variations occur in the different series. Thus the paraffins, mono- and polyhydroxy-compounds, or alcohols, give relatively higher results than the aldehyds, fatty oxides, and ethereal salts. Formic acid and its ethylic salt being exceptional, as in the case of the rotations.

These fluctuations in the refractions must, therefore, be real, and not due to experimental errors, and the influences modified as in the rotation, by molecular arrangement, the so-called value used in calculations being only the average influences which the elements exert in different compounds. These must not be regarded as physical constants.

It is at present impossible to determine with certainty the relationship of these influences to the true value of the elements, especially as there are few elements suitable

for examination, and even these are usually molecular groups, but the evidence, though scanty, points to the probability of the true values of the elements not being largely different from the average influence they exert in the ordinary saturated carbon compounds, though perhaps rather higher.

In saturated cyclic compounds the structure is, as might be expected, also simple, and like that of ordinary open chain compounds, because the influence of the CH_2 groups contained in both is apparently practically the same. But directly unsaturated groups occur in open chain compounds, and consequently greater molecular complexity of the molecule exists, larger rotations and higher refractive power manifest themselves, and these increase with each repetition of the unsaturated group, notwithstanding that there is a loss of H_2 in composition each time. When, however, these unsaturated groups are united, so as to form a cyclic compound, a much greater effect is produced, both on rotation and refraction, evidently due to the formation of a new molecular system.

Considering these products from the saturated to the unsaturated, and then to the cyclic condition, each step being accompanied with a reduction of H_2 , and at the same time a rise in rotation and refraction, and then a still larger increase on the formation of the nucleus, it becomes evident that it is the increase of molecular complexity that is the cause of the augmentation of these properties, and that it is not the composition of the substance which produces the effect. It would be difficult to believe that the true rotation or refractive power of an element could be a variable quantity.

Whilst the influences given for the rotations and refractive power of the elements in the fatty series are not true values, yet this does not militate against their usefulness as a means of judging the constitution of compounds. The same is also true of the apparent values of phenyl and the effect of other groups in the aromatic series.

74. "Mononitroguaiacol." By RAPHAEL MELDOLA, F.R.S.

In the course of some investigations on phenol derivatives, not yet complete, the author had occasion to prepare mononitroguaiacol. As this compound does not appear to have been described before, and as the author learns that other investigators are engaged on the same subject, the following note on the method of preparation may be found of use. The difficulty in nitrating guaiacol directly is to prevent the nitration going too far, so as to avoid the formation of dinitroguaiacol on the one hand, or, on the other hand, complete destruction of material. The action of nitric acid on guaiacol is rendered quite manageable by acetylating or benzoylating the compound as a preliminary step. The acetyl derivative is an oil (Tiemann and Koppe, *Ber.*, xiv., 2020); the benzoyl derivative is readily formed by the action of benzoyl chloride on guaiacol in the presence of sodium hydroxide in aqueous solution. Crystallised from dilute alcohol it forms small rhombohedra, melting at $58-59^\circ$. In order to nitrate the acetyl derivative, it is mixed with about an equal volume of glacial acetic acid, and a considerable excess of fuming nitric acid is gradually added to the well-cooled mixture. It is advisable to dilute the nitric acid at first with glacial acetic acid, but the undiluted acid may subsequently be added in small portions, if the contents of the flask are not allowed to become warm. The condition essential for success may be briefly described as being rapid nitration at a low temperature; if allowed to stand too long dinitroguaiacol is formed. The great excess of nitric acid is necessary to form the mononitro-derivative rapidly. The whole operation takes from one and a half to two hours, and the completion of the nitration is best ascertained by stirring a few drops of the solution vigorously with water on a watch-glass. If the oily deposit does not solidify on being stirred with water in the course of a few minutes, more nitric acid is required; when the oily drops soon become crystalline

under the conditions mentioned, the whole contents of the flask must be stirred into cold water in a thin stream, and allowed to stand for some hours. The solid mononitroguaiacol acetate is collected, washed with water, and purified by crystallisation from boiling water. The compound separates on cooling in small, whitish needles, having a melting-point of $101-102^{\circ}$.

0.0985 gave 5.6 c.c. moist nitrogen at 13.5° and 764.8 m.m. = 6.73. The formula $C_6H_3 \cdot NO_2 \cdot OCH_3 \cdot OC_2H_5O$ requires $N=6.63$ per cent.

It is probable that two nitro-derivatives, an ortho- and a para-, are formed during this process, but the orthonitro-compound is present only in small quantity, and is removed by the process of crystallisation. The final product is most probably the paranitro-compound, $C_6H_3 \cdot NO_2 \cdot OCH_3 \cdot OH$ (4:2:1), for reasons that will appear subsequently. The acetyl derivative is readily hydrolysed by boiling with dilute caustic alkali for a few minutes. An orange solution of the alkaline salt of nitroguaiacol is obtained, and, on acidifying, the nitroguaiacol separates out in the form of whitish ochreous needles. After purification by crystallisation from hot water, it has a melting point of 104° .

0.0732 gave 5 c.c. moist nitrogen at 12° and 771.2 m.m. = 8.22. The formula $C_6H_3 \cdot NO_2 \cdot OCH_3 \cdot OH$ requires $N=8.27$ per cent.

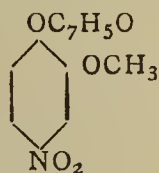
Benzoylguaiacol is nitrated in acetic acid by the same method as that described for the acetyl derivative, and, on the whole is a more satisfactory compound to work with. The first action of the nitric acid is the formation of an oily product, which does not solidify in water, possibly a nitrate. When sufficient nitric acid has been added, the oily deposit solidifies in water, as before, but vigorous stirring on the watch-glass is necessary to promote crystallisation. The benzoylnitroguaiacol thus obtained consists of a mixture of two modifications, which can be separated by crystallisation from alcohol. The chief product, which separates out first, consists of prismatic needles, melting at $102-103^{\circ}$. The mother-liquor deposits the other modification on standing, in the form of rhombic plates, which, after two or three crystallisations from alcohol, have a melting-point of $88-89^{\circ}$.

0.0976 (needles) gave 4.15 c.c. moist nitrogen at 14.5° and 765.9 m.m. = 5.01.

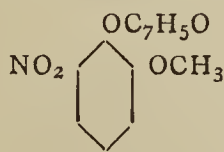
0.1078 (plates) gave 4.8 c.c. moist nitrogen at 19° and 764.1 m.m. = 5.12.

The formula $C_6H_3 \cdot NO_2 \cdot OCH_3 \cdot OC_7H_5O$ requires $N=5.12$ per cent.

Although no direct proof of the constitution of these two nitro-derivatives has been obtained as yet, there is every reason for believing that they are the ortho- and para-compounds.



M. p. $109-103^{\circ}$.



M. p. $88-89^{\circ}$.

This view, so far as relates to the para-compound, is borne out by the fact that the nitro-guaiacol of m. p. 104° obtained by the hydrolysis of the acetyl derivative of m. p. $101-102^{\circ}$, gives the same benzoyl derivative (m. p. $102-103^{\circ}$) on treatment with benzoyl chloride and alkali in the usual way. It may be pointed out that the paranitro-derivative has been prepared more especially with a view to the direct synthesis of eugenol and related compounds, since the replacement of the nitro-group by halogens, and subsequently by allyl, should give rise to the formation of benzoyleugenol.

In carrying out these experiments much valuable assistance has been rendered by Mr. Edward J. Wray.

NOTICES OF BOOKS.

Kelly's Directory of Chemists and Druggists. This work includes Manufacturing Chemists, Wholesale Druggists, Drysalter, Patent Medicine Vendors, and other Trades connected therewith, of England, Scotland, and Wales, and most of the Principal Towns in Ireland. Eighth Edition. London: Kelly and Co., Ltd. 1896. 8vo. Pp. 807.

We must pronounce this Directory very useful, both from our own examination and from information which reaches us through private channels. At the same time, whilst fully aware that Messrs. Kelly must know their own business best, we cannot help thinking the arrangement of trades and professions here adopted very singular. Supposing that analytical and consulting chemists, assayers, and chemical manufacturers should be associated with the chemists and druggists, we do not see why hospitals, photographers, dealers in "patent" medicines, dentists, and veterinary surgeons should be here included. These two bodies might, we submit, be more suitably introduced into a medical directory, whilst certain other trades which figure here would be more at home in a "Quack Directory," if such a work could be safely or justifiably published. The photographers might perhaps better figure in an Art Directory. Perhaps such arrangements might occasion an excess of matter in some of Messrs. Kelly's Directories, and a deficiency in others.

Chemistry in Daily Life: Popular Lectures. By Dr. LASSAR-COHN. Translated by M. M. PATTISON MUIR, M.A., Fellow of Gonville and Caius College, Cambridge. With 21 Woodcuts in the Text. London: H. Grevel and Co. 1896. Pp. 324.

THIS book reminds us, by its title, very closely of a work of British origin which has met with general approval and has gone through several editions. Prof. Pattison Muir observes, in his Preface, that "chemistry is emphatically the most human, and for that reason the most fascinating, of the Sciences,"—an assertion which will not be universally admitted. "Vague notions," the translator tells us, "circulate in men's minds concerning chemistry. Some think the chemist is a man who compounds drugs and mixes pills,"—an error, we must add, exclusively British. The dispenser of medicines is called in France "pharmacien," and in Germany "apotheker."

The author sets out with respiration, the maintenance of animal heat and combustion, passing on to flame, candles, the elements, chemical formulæ, atoms and molecules, coal-gas and the nature of flame.

The third chapter introduces us to the chemistry of agriculture, to the diet of men and other animals, fibrin, serum, artificial fodder, and gelatin.

In the fourth lecture we are taught the importance of a mixed diet, to the question of bounties on exported sugar—a procedure by which several Continental countries waged, and still wage, a war against Britain.

In the fifth lecture we find an account of the dietetic values of the chief foods, of fermentation, and the various alcohols.

In dealing with these subjects Prof. Lassar-Cohn has not been able entirely to avoid stroking the vegetarians and the "temperance" party against the grain. (See p. 119).

In the sixth lecture we pass to vinegar, wood-spirit, and the Greek fire, gun-cotton, which the author admits has come out victorious in all contests with melinite, which is not much spoken of. Dynamite is said to have come into favour for the peaceful purpose of mining, and also, it might have been added, for the operations of socialists, anarchists, and nihilists. Blasting gelatin, the mixture of gun-cotton in nitro-glycerin, is rightly pronounced the most energetic explosive at our disposal.

From explosives Prof. Lassar-Cohn takes a leap to clothing materials, speaking of shoddy and mungo as artificial wool—a rather misleading expression. Tanning comes next in its various modifications, such as chrome- and iron-tanning. The leathers obtained by these two procedures have not given satisfaction in Europe, though a chrome-leather is still produced in America.

Bleaching and dyeing next engage the reader. Prof. Lassar-Cohn seems to hope that artificial indigo may yet be produced cheaply enough to compete with or supersede the natural colour, an aspiration in which we by no means share.

In the latter part of the book we find, among other things, a dissertation upon bimetalism, strangely out of place. The Röntgen rays are also described, so are also the modern disinfectants and the ammonia process for the manufacture of soda, though without any mention of its first discoverers.

The defect of this work, as far as English readers are concerned, is its predominating German point of view, *e.g.*, the remarks on beet-sugar, on rye-bread, &c. In other respects the book will prove valuable and instructive.

Water Supply (considered principally from a Sanitary Standpoint). By WILLIAM P. MASON, Professor of Chemistry, Rensselaer Polytechnic Institute; Member of American Philosophical Society, American Chemical Society, American Water-Works Association, New England Water-Works Association, Franklin Institute, &c. First Edition; first thousand. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1896. 8vo.

We have here a work of very considerable value. With the increase of population, especially in the river valleys and the collecting area whence the streams must receive their supplies, the difficulty of obtaining an adequate quantity of a trustworthy water has increased, and must still further increase.

Our author, in his introductory chapter, fully appreciates the abundance and the excellence of the water supplied to ancient Rome.

The second chapter treats of drinking-water and disease. The connection between bad water and certain of the most alarming types of disease is no longer open to discussion, but the question still exists—What waters are to be regarded as bad? Swamp waters, such as those of the Dismal Swamp of Virginia, and the *aguas negras* of certain affluents of the Orinoco, though loaded with dissolved organic matter, are not found to occasion troubles, whilst the beautifully clear waters from certain wells in London (now disused), and the drainage from the rice-fields of India, are almost more than dangerous. According to Schröder, here quoted, peat-dust kills the spirillum of cholera in five hours. Laveran concludes, from his experience, that travellers in malarial districts find that they may very generally escape intermittents by boiling the drinking-water. The authorities here quoted are far from considering polluted water the only channel for the malarial poison. African friends tell us that in certain districts the water-melons are full of malaria, and caution new-comers against their use. The presence of decomposing sawdust in streams is pronounced by Dr. Mulhern, of the Michigan Board of Health, a source of malaria. Parke's "Hygiene" is quoted to show that dangerous waters may be made safe by a previous treatment with alum. The ground seeds of *Stychnos potatorum* are successfully used for the same purpose in tropical Asia and Africa. The celebrated Lausen case is here cited, and is valuable as showing that the passage of foul waters over or through soil is no sure method for their purification.

The account given (pp. 48 to 51) of the disease spread by the great pilgrimages in India is horrifying. But the

case concerning the sanitary state of China is much worse than our author makes it appear.

In a note the author recognises the fact that common flies may aid in distributing cholera. This holds good with the zymotic diseases.

Mr. Mason's work is a storehouse of facts interesting to the sanitarian, and deserves a very wide circulation. The only error which we find in it is the statement that the notorious "Recommendations" of the late Rivers' Pollution Commission in this country now form part and parcel of British sanitary law.

CORRESPONDENCE.

ON THE SPECTRAL AND OTHER PROPERTIES OF THALLIUM IN RELATION TO THE GENESIS OF THE ELEMENTS.

To the Editor of the Chemical News.

SIR,—The posthumous publication, in successive numbers of the CHEMICAL NEWS from October last to the present month, of the Spectroscopic Studies of Jean Servais Stas, is opportune in view of the strong conviction which now prevails in the minds of many eminent chemists and physicists, that the elements have been evolved from a primordial substance of small specific gravity and of low atomic weight.

The avowed object of the distinguished Belgian chemist in undertaking these studies, as stated in his "Introduction," was to ascertain whether he could cause, by increasing the temperature or the intensity of the electric current, a correlation among the characteristic bands of the luminous spectra of compounds of the alkaline and alkaline-earth metals and of thallium, when these elements were in a state of purity.

That Stas entered upon these investigations with some degree of prejudice, and with full assurance that his non-success should be the measure of the power of all future investigators, will be evident from his own statement that "I was well aware that if my experiments failed, after having taken great pains and having devoted to this work an amount of time which I might, perhaps, have used more profitably, I should add nothing to the sum of our spectroscopic knowledge. Still, I should free Science from an hypothesis which has led astray, and may again lead astray, many clever men; it seemed to me that this was just as much helping to advance *real* knowledge."

Experimental researches undertaken in this spirit, as might have been expected, were purely negative in their results; and as some of them are in direct contradiction to those of other investigators, the interests of Science demand that these discrepancies should not be allowed to pass unnoticed.

Since the publication of my paper "On the Origin of Elementary Substances" (CHEMICAL NEWS, vol. xxxviii., p. 66), I have made many experiments on the spectra of the elements, through great ranges of temperature and pressure, with the object of effecting their mutual transformations, but hitherto without any positive result. Nevertheless, my failure to effect such spectral transformations has not diminished my belief in the ultimate solution of the problem; still less so in the theory that elementary species have been formed by the successive condensations of a primordial substance of great tenuity. No naturalist of reputation is now to be found who rejects the doctrine of the evolution of organic species from a few simple forms, on the ground that the transformation of one natural species of plant or animal into another has not so far come under man's observation. Moreover, just as the evolutionary theory of organic species derives its chief support from the artificial variations induced in plants and animals under domes-

tication, so the theory of the evolution of elementary species from a few typical elements is equally well supported through the power of modern chemists to form homologous series of the positive and negative organic radicals, which possess properties similar to those of the elements.

The spectroscopic research on thallium undertaken by Stas to disprove the doctrine of the transformation of elementary substances is interesting as showing how a distinguished chemist, with all the wealth of chemical and physical appliances at his disposal, should himself have missed the road which he expressed so much anxiety for other investigators to follow.

Long before the researches of Stas, the spark spectrum of thallium had been examined by Huggins and by Thalén. The arc spectrum of this metal has also been mapped by Liveing and Dewar, and by other investigators, far into the ultra-violet. My own researches on the spectrum of thallium, at different temperatures and from a millimetre to 80 atmospheres of pressure, led to the discovery in the arc and spark spectrum of the red line, 6560 (*Proc. Roy. Soc.*, April 20, 1893).

The discovery of this line directly correlated the spectrum of thallium with the homologous spectra of indium and gallium, and furnished the most instructive example of the mutual dependence of the properties of elements of the same series (indicating a community of origin) that is to be found in the whole range of the physico-chemical sciences.

It is now common knowledge that, within the limits of the infra-red and ultra-violet, thallium has three distinct spectra of temperature:—

1. The flame spectrum, consisting of a single green line, 5349.
2. The arc spectrum of two lines, 6560 and 5349.
3. The spark spectrum, with lines 6560, 5949, 5349, 5153, 5078, 5053, 4981, and other lines less characteristic.

Now the final result of the elaborate study of the spectrum of thallium by Stas, as stated by himself, is "that the electric spectrum of thallium consists of a single green line not capable of being split up, exactly like the flame spectrum of this metal, and that *electricity is no more capable of dissociating it than heat.*" (The italics are as printed in the *CHEMICAL NEWS*). We have in this conclusion a direct contradiction of the results of other competent observers who have examined the spectrum of thallium. Stas would appear to have felt this difficulty, by suggesting that the spark spectrum in air may not be that of the pure metal, but of its oxide.

To set at rest the doubt thus raised, I have recently examined the spark spectrum of metallic thallium in nitrogen, produced by passing atmospheric air over red-hot copper and dried over sulphuric acid, when I found the spectrum to be the same as that obtained in air. I would here remark that the red line, 6560, of the arc spectrum is somewhat elusive, unless there is a sufficient quantity of the metal in the crater of the arc to reverse the green line, when the red line invariably shines out with marked brilliancy in all the specimens of the metal, its sulphate, carbonate, nitrate, and chloride, which I have experimented with. It is also advantageous to fill the crater with the metal, or its compounds, before the arc is struck, in order to ensure an abundance of thallic vapour during the observation.

Another method adopted by the Belgian chemist to discredit the results obtained by other investigators of the spectrum of thallium, is to be seen in his statement that "since observers have found a complex electric spectrum of thallium when using thallium they have not prepared themselves, I think I am correct in concluding that the metal they used was other than that used by Bunsen, Lecoq de Boisbaudran, and myself."

Now as there are many workers in science who, from education and habit, may still look to Stas as an authority on questions relating to spectral analysis, the multiple

relations of the atomic weights, and the genesis of the elements, I will now offer the sum of £50 to any chemist who will submit a specimen of pure thallium (not less than a cubic centimetre) which will only show the green line 5349 in the electric spectrum; and I will also contribute, on the same condition, a further sum of £100 to the Research Fund of the Chemical Society; the specimens of thallium to be tested either at the laboratories of the Owens College, or at the house of the Literary and Philosophical Society, Manchester.—I am, &c.,

HENRY WILDE.

Alderley Edge, June 19, 1896.

DOES HYDROGEN FIND ITS PROPER PLACE AT THE HEAD OF GROUP I. OR AT THE HEAD OF GROUP VII.?

To the Editor of the Chemical News.

SIR,—In reference to the interesting paper by Professor Orme Masson contained in the last number of your valuable journal, may I be permitted to make a short quotation from a note of mine published in the *CHEMICAL NEWS* of July 12th, 1872 (vol. xxvi., p. 19):—

"Hydrogen and chlorine are here classed together on account of their mutual replaceability, with but a slight change of properties, in many chemical compounds, such as trichloroacetic acid, &c. The position, too, of hydrogen in the list of elements when arranged in the order of atomic weights, indicates that it is really the lowest member of the chlorine group."—I am, &c.,

JOHN A. R. NEWLANDS.

Laboratory, 27, Mincing Lane, E.C.,
June 23rd, 1896.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cxxii., No. 22, June 1, 1896.

The President announced the death of M. Daubrée, the *doyen* of the Section of Mineralogy. It will not be forgotten that one of his constant observations was the description and classification of meteorites of every kind.

Action of Acetylene upon Iron, Nickel, and Cobalt reduced by Hydrogen.—Henri Moissan and Ch. Moureu.—Will be inserted in full.

The Respiratory Exchanges in the case of Muscular contractions occasioned Electrically in Animals Fasting or Fed upon Rations rich in Carbohydrates. Corollaries referring to the Determination of the Potential directly devoted to the Physiological Work of the Muscles.—A. Chaveau and F. Laularié.—The potential devoted to the execution of muscular work is always a carbohydrate, either borrowed from the reserves of glycogen of the organism, or coming from the transformation of the fatty reserves or furnished more or less directly to the muscles of the digestive absorption.

On Molybdenite and its Preparation with Molybdenum.—M. Guichard.—Will be inserted in full.

On the Methylamines. — M. Delépine. — Nessler's reagent gives with dimethylamine and trimethylamine a white precipitate which disappears on the addition of water. On the contrary, it gives with monomethylamine a light yellow precipitate, which is formed with great sensibility and which re-dissolves neither in an excess of water nor in an excess of the reagent. Sulphuric acid

dissolves it in heat, and on dilution it reappears if the heat has not been too prolonged. It blackens easily on exposure to light.

On the Phenylhydrazine Aldehydates.—H. Causse.—An account of the aldehydates of diphenylhydrazine and the benzylate of the same base.

Ceramic Stones obtained by the Devitrification of Glass.—M. Garhey.—The author uses especially bottle-glass and window-glass containing an excess of earthy bases. These materials are pulverised and devitrified by successive treatment in two furnaces. In the first furnace, which has a lower temperature, they remain for an hour, and in the second, which is much hotter, they are left for a few minutes only.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 5, Vol. i., No. 3.

Report presented by H. Le Chatelier on the recent Work of Richards on Aluminium. Submitted on behalf of the Committee of the Chemical Arts.—As a solder for aluminium, Prof. Richards particularly recommends a mixture of—

Aluminium	2 parts.
Zinc	26 "
Tin	70 "
Tin phosphide	2 "

100

It should be applied without flux upon the article, previously roughened and heated, if possible above the melting-point of the solder. The alloys of aluminium with gold have a fine red colour, and are utilised in jewellery; their melting-point has been studied by Prof. Austen. Among the alloys of nickel, mention is due to "roseine" consisting of—Nickel, 40; aluminium, 30; tin, 20; silver, 10. The alloy "manganine" consists of—Copper, 67.5; aluminium, 1.2; manganese, 18; zinc, 13; tin, 5; it is remarkable for its high electric resistance, which is superior to that of German silver. Its tenacity is 25 kilos. for 1 square millimetre. The ternary alloys, containing both nickel and copper, are remarkable for their mechanical properties.

Cu	88	90	64
Ni	1	3	33
Al	1	3	3
Sn	1	6	0

The two former have a tenacity of 60 kilos. per square millimetre. The third has a superior tenacity. It is suitable for the manufacture of table cutlery.

NOTES AND QUERIES.

* * Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Fluor Spar.—A correspondent wishes to know the approximate annual consumption of this mineral, the present price, and whether the English or foreign product is mostly used, and which is the better quality.

German Dictionary.—Can any correspondent recommend a German Dictionary suitable for use with German scientific literature.—IGNORAMUS.

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Gmelin's Handbook of Chemistry (Organic and Inorganic), by HV. WATTS, complete set, 19 vols. cl., scarce, £20. for £8 8s.
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SESSION 1896-97.

The Courses of Instruction in ENGINEERING and CHEMISTRY at the Institute's Colleges commence in October, and cover a period of two to three years. The MATRICULATION EXAMINATION of the CENTRAL TECHNICAL COLLEGE will be held on September 21st to 24th, and the ENTRANCE EXAMINATION of the Day Department of the TECHNICAL COLLEGE, FINSBURY, on September 22nd.

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JOHN WATNEY,
Hon. Secretary.

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SESSION 1896-97.

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